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INVESTIGATIONS OF INFRA-RED SPECTRA

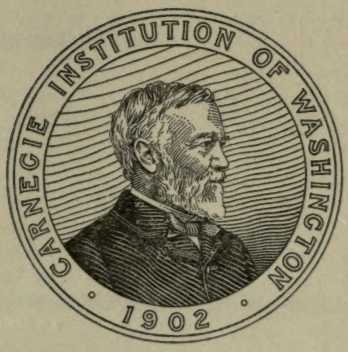
[Vol. 2.]

Part III—Infra-Red Transmission Spectra

Part IV—Infra-Red Reflection Spectra

BY

WILLIAM W. COBLENTZ



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PREFATORY NOTE.

Parts I and II of "Investigations of Infra-red Spectra" were published by the Carnegie Institution of Washington, October, 1905.

The present volume contains the detailed results of a continuation of this work carried on at the National Bureau of Standards during the past year.

PART III

INFRA-RED TRANSMISSION SPECTRA

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CHAPTER I.

INTRODUCTION.

In the various determinations of the physical properties of matter, such as electrical and thermal conductivity, specific inductive capacity, coefficients of expansion and refraction, etc., the spectroscopic study of the transparency of substances to radiant energy, and in particular to heat-waves, has been left in the background, although this data is just as necessary in meteorology, geology, and the allied sciences as is our knowledge of any of the other so-called constants of nature.

The following research was undertaken to ascertain the cause of absorption, and the connection between absorption and the structure of crystals. In this and in a previous research it has been shown that certain absorption bands in the infra-red are due to particular groups of atoms. The relation of these results to the question of the structure of crystals will be obvious to the reader. For, if the crystal is composed of molecules of, say, water and calcium sulphate, which separately have characteristic absorption bands, then, if these molecules or certain groups of atoms in them undergo no physical change when they combine to form a crystal (of selenite in this case), one would naturally infer that the absorption spectrum of the product will be the composite of the absorption bands of the two constituents.

This phenomenon is different from the one in which Julius[1] showed that the absorption spectrum of a chemical compound is *not* the composite of the bands of the constituent elements. Here the physical molecule has been changed.

Just how these specific groups of atoms are placed with respect to the crystallographic axes it is impossible to determine.

A practical question in optics, viz, the possibility of finding material suitable for prisms, in certain regions of the spectrum in which our present prism material is opaque or in which its dispersion is small, was also kept in view.

The reflecting power of metals was included to fill a gap left in the work of Hagen and Rubens done at the Physikalische Technische Reichsanstalt. The reflection from minerals composing the earth's crust has unexpectedly furnished us with data which will be useful to the meteorologist. It may even aid in clearing up such an obscure question

[1] Julius: Verhandl. Konikl. Akad. Amsterdam, Deel I, No. 1, 1892.

as the radiation from the moon. The exact determination of the data presented involves the use of one of the most sensitive heat-measuring devices yet produced, viz, the radiometer. The region examined is a vast one compared with the visible spectrum, and has heretofore been little explored.

From the intimate relation between refractive index and reflecting power, the data obtained gives us some idea of the dispersion of the substances examined. The bands of selective reflection, especially the very sharp ones, such as the new one found in quartz at 12.5 μ, will be useful as a monochromatic source of energy, for example, in interferometer work.

Many chemical compounds contain both oxygen and hydrogen, which, on applying heat, pass off in the form of water. That the water is not united so tenaciously as the other constituents is evident from the fact that in many instances it can be more easily removed; many salts give up their water if exposed to dry air at ordinary temperature. From the circumstance that many of these compounds are crystalline, the water is said to be present as *"water of crystallization."* The manner in which the water exists in the crystal is not understood. By some it is considered a part of the chemical molecule; by others it is thought that the molecules of water exist in their entirety among the molecules which constitute the crystal. It is characteristic of water of crystallization that it is expelled at a temperature far below red heat, and frequently below 100° C. Another characteristic of minerals containing water of crystallization is their property of reabsorbing water after it has been removed. Copper sulphate is an excellent example; on applying heat, the blue crystal becomes a crumbling white mass, which, if permitted to stand in dry air, absorbs water and resumes its blue color and crystalline structure.

On the other hand, the water which is given off only at a red, or even a white heat, can scarcely be present in the compound in the same manner as the water of crystallization, and is distinguished as *"water of constitution."* In this case the water is not supposed to exist as such in the mineral, but to result from the union of oxygen and hydrogen or from the hydroxyl groups contained in the compound.

Of course there are minerals which contain water in both these forms. In copper sulphate ($CuSO_4+5H_2O$), four molecules of water are given off at 100° and the fifth at 200°, so that the latter is possibly combined in some manner different from the former. In epsomite ($MgSO_4+7H_2O$), six molecules of water are given off at 132°, while

the seventh is held more tenaciously, and is not given off until heated to 210°.

However, in cases like these, where successive portions of water are given off at different temperatures, it is difficult to make a distinction between water of crystallization and water of constitution. In the minerals just quoted, however, it has been found that the heat of hydration of the last molecule of water is different from that of the molecules of water which pass off at a lower temperature, which confirms the belief of a difference in the bonding in the two cases.

As a whole, the question of the association of the atoms of oxygen and hydrogen in certain compounds is far from settled, while the difficulties involved in its investigation are very great. The existing data bearing upon the subject is practically nil.

PRESENT METHOD OF INVESTIGATION.

In a preliminary paper bearing upon this subject[1] the writer described the infra-red absorption spectra of two numerals, selenite ($CaSO_4 + 2H_2O$) and brucite ($Mg(OH)_2$), in which the atoms of oxygen and of hydrogen are thought to be combined in a different manner. It was the application of the results of previous work, in which it was abundantly proven that certain groups of atoms have characteristic absorption bands. Hence, if the oxygen and hydrogen, which enter into the composition of certain minerals, are united as they are in a molecule of water, then one would expect to find the absorption spectra of such minerals to be a composite of the bands of water and of the bands caused by the other constituents.

The only previous investigation bearing on this subject, from the standpoint of infra-red absorption spectra, is that of Königsberger,[2] who studied the pleochroism of several minerals, including selenite. Unfortunately his plate of selenite was too thick, so that no energy was transmitted beyond 2.5 μ. He calls attention to the fact that a small absorption band at 1.5 μ coincides with that of water, from which it would appear that in selenite the absorption of the "water of crystallization" does not appear to be different from that of water.

Thinking that it would be fairer to select the *large* water bands at 3.0, 4.75, and 6 μ as a criterion, the writer (loc. cit.) examined thin sections of several minerals and found, as had been anticipated, that minerals containing water of crystallization have large absorption bands

[1] Physical Review, 20, p. 252, 1905.

[2] Königsberger: Ann. der Phys., 61, p. 703, 1897.

coinciding with those of water. The selection of selenite ($CaSO_4 + 2H_2O$) and brucite ($Mg(OH)_2$) as types of water of crystallization and of constitution was a fortunate one, for the two following reasons: (1) The selenite curve showed all of the absorption bands of water in their proper positions and intensities, except the 4.65 μ band, which is shifted and too deep for the thickness of water contained in the plate under examination. The fact that the band is shifted caused me to suspect that it may be complex, and, from the fact that it lies in the region where the NCS radical and certain sulphur compounds have a strong absorption band, that it may be due to the SO_4 radical—a surmise that since then has been unexpectedly verified. (2) Although the brucite curve did not contain the water bands, thus showing the difference between water of constitution and water of crystallization, it contradicted my previous work,[1] in which it was shown that the OH radical in the alcohols has an absorption band of 2.95 μ (true value is 3 μ). From the brucite curve the conclusion was drawn that the OH radical is inactive. Since then I have studied the chemical side of the question more thoroughly, from which it appears that there is no marked difference[2] in the activity of the OH radical in the hydroxides studied, and, hence, that the brucite curve should have a band at 3.0 μ instead of the one shifted to 2.5 μ. In other words, the present research, which is in part the outcome of the foregoing discrepancies, has to a very unexpected degree furnished us with an abundance of new proof that certain groups of atoms have definite absorption bands, which really means that these groups of atoms, or "ions," enter into the various compounds in a similar manner.

To sum up, in the present investigation the criterion for distinguishing water of crystallization from water of constitution is the presence of absorption bands at 1.5, 2, 3, 4.75, and 6 μ, which is the location of the absorption bands of water. If there are no other absorption bands near by, then the intensity of these bands should be somewhat like that of water, viz, the bands at 1.5, 2, and 4.75 μ are weak, while the bands at 3 and 6 μ are very strong.

A hydroxyl group will also cause an absorption band at 3 μ. Silicates may have a small band shifting from 2.9 to 3.1 μ, but since it is weak, there is no danger of confusing it with the strong water band in the same region.

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[1] Investigations of Infra-red Spectra, Washington, 1905; Phys. Rev., vol. 22, 1905.

[2] From the chemical standpoint, however, the OH in alcohol and in H_2SO_4 is more active, since it is replaceable by a metal (more acid) than the OH in brucite ($MgO(OH)_2$), which is not replaceable (more basic).

PLEOCHROISM.

Since the present research involves the examination of minerals which are not isotropic, the question presents itself whether it would be better to examine them in natural or polarized light. In the former case we obtain *all* the absorption bands, irrespective of the direction of transmission, but their observed intensities will not necessarily be real. In the latter case, where the intensity of the transmitted energy depends upon the direction of vibration of the polarized rays with respect to the axes of the crystal (pleochroism), the observed intensities will be real, the number and position of the absorption bands will depend upon the direction of observation, but the accuracy is less the farther one penetrates the infra-red, due to loss in polarizing the source of energy.

By these statements it is not intended to give the impression that pleochroism is not worth considering. The work of Merritt[1] and of Königsberger[2] is especially valuable in demonstrating that absorption is dependent upon the direction of vibration of the incident energy. The visible spectrum is so narrow that it is difficult to separate the absorption bands, while, on the other hand, the infra-red is a vast and almost unexplored region, and it is here that one would expect to resolve wide absorption bands such as exist in the visible spectrum. The curves of Merritt and of Königsberger show this, especially the calcite curves, which are entirely independent for the ordinary and extraordinary rays. Nevertheless, in looking over the previous work, it seemed to the writer that in the present state of our knowledge of absorption a greater advance would be made by simply mapping the spectra of a great many minerals for energy transmitted through them in its natural mode of vibration.

The results have been most gratifying. If we had been content with the examination of a few, easily obtainable, large-sized crystals like colemanite, for pleochroism, the results would have been quite different.

The maxima of the absorption of water are constant in position for the amorphous and the crystalline minerals studied, which would indicate that in this case the transmission is not affected by the direction of vibration.

The desirability of examining many minerals is illustrated in the appended curves, in which it will be seen that frequently in one region of the spectrum the water bands are obliterated by an increase in the general absorption or by an adjacent absorption band, while in another part of the spectrum the water bands are very distinct.

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[1] Merritt: Phys. Rev., 2, p. 424, 1894.

[2] Königsberger: Ann. der Phys., 61, p. 687, 1897.

APPARATUS AND METHODS.

In the present investigation a mirror spectrometer, a rock-salt prism, and a Nichols radiometer were used. With the exception of certain improvements, the details in mounting and adjusting the different parts have been described elsewhere,[1] and it will be sufficient to add that the spectrometer mirrors were 10 cm. in diameter and 50 cm. in focal length, and that the rock-salt prism was an unusually fine one having a refracting angle of 59° 59′ 36″ and faces 9 by 9 cm. area. The spectrometer slits were 0.3 mm. wide, or about 2′ of arc. The time required for the radiometer to reach a maximum deflection was about 20 seconds. The different portions of the spectrum were projected upon the radiometer slit by using the Wadsworth[2] mirror-prism method and rotating the prism-table. Although one doubles the error in making spectrometer settings, the method was the most convenient one in the present work. The "heater" of a 110 Nernst lamp on an 80-volt storage-battery circuit was used as a source of energy. The sections were mounted in the usual manner upon a wooden carrier which moved in vertical ways between the source of energy and the collimator slit.

To protect the prism from moisture a small crystallizing dish of phosphorus pentoxide was placed over it, and when not in use a large glass crystallizing dish was inverted over the prism and drying material. The edge of the large dish was ground to fit the prism-table and prevented the entrance of moisture.

The spectrometer was remodeled from a small Fuess pattern having mirrors 4 cm. in diameter. The focal length of the new mirrors was selected as being more advantageous than the 35 cm. or 100 cm. mirrors, used in previous work, on account of the increased resolving power over the former and the decreased atmospheric absorption which is apparent in the latter. The advantages gained by the use of the larger prism and mirrors is so much more than anticipated that it seems worth while to mention it here. The whole was inclosed in a tin box to protect the prism from air currents and from moisture.

The radiometer was of the usual form, with an additional improvement which consisted in covering it with a piece of heavy brass tubing, within which was a thick layer of hair felt. Although the radiometer stood close to a large outside window and exposed to sunlight, it was not affected by temperature changes. The vanes were of mica, covered with copper oxide, which was applied by means of shellac or a thin

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[1] Phys. Rev., vols. 16 and 17, 1903; Investigations of Infra-red Spectra, Washington, 1905.

[2] Wadsworth: Phil. Mag. (5), 38, p. 346, 1894.

layer of Canada balsam. This method of blackening the vanes was found easier and more satisfactory than smoking them.

The sensitiveness was about 10 cm. deflection per square millimeter of exposed surface, scale and candle at 1 meter. The weight was 10 milligrams. The vane was made heavy to avoid tremors.

ACCURACY ATTAINABLE.

The writer has been so frequently questioned on the accuracy of the observations that a few remarks will be in order.

First of all, nearly all the substances examined have numerous absorption bands, so that we can not find an extinction coefficient by means of which we may determine their transmissivity in absolute value for, say, a centimeter thickness. Again, different samples of a given mineral will vary in homogeneity and in purity. Different parts of a given specimen will vary in thickness, homogeneity, purity, and polish, so that, on remounting the same sample before the spectrometer slit, the relative values of transmission may differ by several per cent. The result is that such a comparison has but little meaning, and is at all times of minor importance. But, after once mounting the specimen before the spectrometer slit, the important question is the relative transparency of different regions of the spectrum and the accuracy of the location of the maxima of absorption. This depends upon the accuracy of the observations in any region of the spectrum. With a trustworthy instrument like the radiometer, and with the specimens securely mounted before the spectrometer slit, in the present research it was found that for a given spectrometer setting the variation of single observations would differ from the mean by only about a tenth of 1 per cent, so that only in the extreme infra-red, or in locating sharp maxima, were the observations repeated. Consequently the reality of many of the small maxima can be accepted with confidence. The most important question, however, is the accuracy of the location of the maxima, especially those which are sharp and well defined.

During the past few years the writer has repeatedly mounted and adjusted his apparatus and has always found the location of certain sharp absorption and emission bands, used as standards of reference, to agree to 0.02 μ, which is as accurate as our knowledge of the dispersion of rock salt will permit. The adjustment of the zero of the instrument was tested daily. It was found that the yellow helium line is narrower and brighter and thus better adapted than sodium for making this setting.

PREPARATION OF THE MINERAL SECTIONS.

Whenever possible the crystals were split parallel to a cleavage plane, since many crystals would break in grinding. The remaining ones were ground thin in the ordinary manner. To accomplish this they were mounted upon glass plates by means of pitch having a low melting-point, so as to avoid disturbing the water of crystallization which is expelled from some minerals at a low temperature. The sections were cleaned in chloroform and mounted upon heavy cardboard having rectangular holes about 4 by 10 mm. cut into them. That the crystals were not affected by grinding and the cement was proven in a number of cases where cleavage sections of the same mineral were examined. Sometimes the sections were mere fragments 5 mm. long, so that two pieces had to be placed end to end with a slight overlapping, but not glued at the center. Since we are not concerned with total transmission, but simply with absorption bands, this does not interfere with the investigation. Of course if a glue could have been found which is free from large absorption bands, the sections could have been mounted upon rock-salt plates and ground much thinner. As it was, the sections were entirely free, except at the ends, which rested upon the cardboard, which was then mounted upon the holder, which moved in vertical ways before the spectrometer slit.

In the description of the different minerals, the direction of cutting the sections is parallel or perpendicular to some crystallographic axis. In many crystals there is usually a perfect cleavage parallel to one of the crystallographic axes, which fact was taken advantage of in preparing the sections. The cleaving was done by means of a small knife-blade struck with a light piece of metal, for example, a file. It may be of interest to note that with crystals, for example anhydrite, which have perfect cleavage in several directions, it was necessary to strike the knife-blade a sudden blow, while in others, like scolecite, a series of light blows started the cleavage and produced large plates. A great many minerals like copper sulphate and alum could not be used, because a slight warming was sufficient to dehydrate them, when the surface became rough and scattered the incident radiation.

In the present research the examination of the sections after being prepared was overshadowed by the difficulty in obtaining specimens of sufficient size and in grinding them thin enough. In my previous work it was found that as a general rule the compounds examined increase in their general absorption beyond 5 μ, so that the (liquid) films had to be reduced to 0.01 mm. In the present work it was impossible to reduce the thickness to much less than 0.1 mm., with the consequent result that many sections became opaque beyond 5 μ.

The minerals were obtained from various dealers and from the U. S. National Museum. They were selected according to composition. Of the total number thus selected only about 40 per cent were obtainable and these were oftentimes the least desirable to illustrate the points in question. The expense involved is no small item, and I am very grateful to Director Stratton for his generosity in meeting that question.

SCOPE OF PRESENT INVESTIGATION.

The principal object in this research was to gain information in regard to the molecular structure of minerals containing oxygen and hydrogen. To this end minerals were selected containing these constituents. Previous work has shown that in organic compounds certain radicals have characteristic absorption bands. One would therefore naturally expect to find similar relations in inorganic compounds, where more important radicals are to be found. Hence, the list was extended so as to contain a series of minerals having the radicals CO_2, PO_4, SO_4 and OH. The results obtained serve the purpose very well for demonstrating the rashness of attempting to establish "laws" from present data for future investigators to refute, just as is being done at present in more thoroughly explored fields, such as, for example, the absorption of solids in solution.

In the study of the carbon compounds in organic chemistry, their constitution has been established by the replacement of certain constituents by organic radicals, by the preparation of a series of derivatives, by vapor density determinations, or by studying their physical properties in solution. Mineralogy is essentially the chemistry of silicon compounds, to which, as yet, it has not been possible to apply any of the above methods, so that the constitution of many minerals has been derived from analogies with other compounds which are better understood. Hence, in an investigation like the present, it is not surprising to find exceptions to the tentative rules for classifying these minerals.

The transmission curves are given without correction for reflection from the surfaces. In most cases, as will be noticed from the reflection curves, the correction is negligible. In one case, viz, stibnite (Sb_2S_3), such a correction is worthy of notice. The transmission shows a uniform value of 45 per cent. To the writer this seemed a very transparent substance until the greater surprise of a uniform reflecting power of about 36 per cent was observed, which indicates that after correcting for reflection this mineral (for the thickness examined) is practically transparent.

CHAPTER II.

TRANSMISSION SPECTRA OF DIFFERENT MINERALS.

GROUP I: MINERALS CONTAINING WATER OF CRYSTALLIZATION.

All the minerals studied which are generally thought to contain water of crystallization are collected in Group I. First of all, it will be necessary to consider the absorption spectrum of water, which has

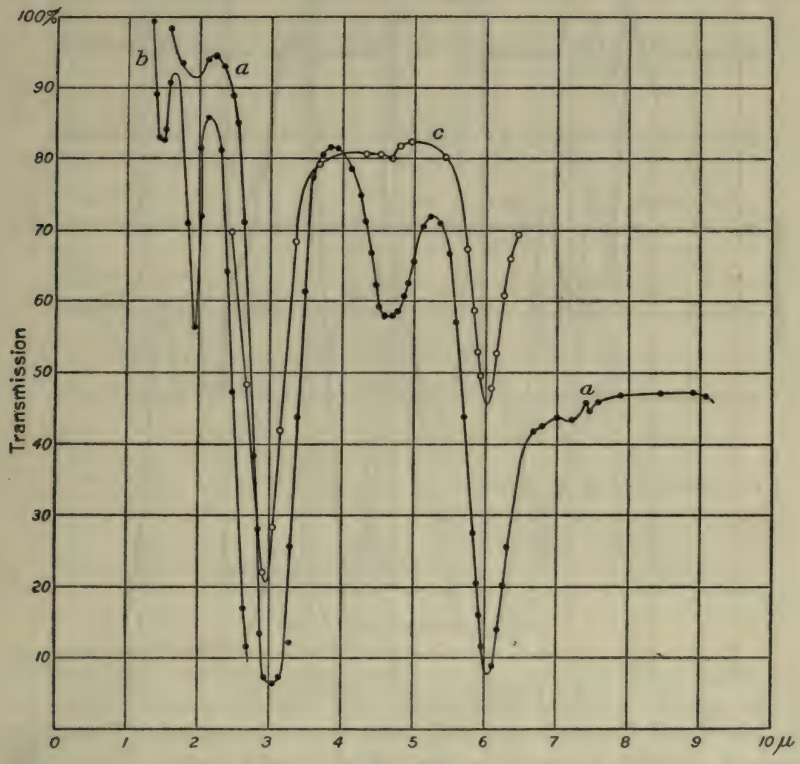

FIG. 1.—Water.

been studied by Julius,[1] Paschen,[2] Aschkinass,[3] and others. All observers agree in their location of large absorption bands at the approximate wave-lengths 1.5 μ, 3 μ, 4.75 μ, and 6 μ.

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[1] Julius: Verhandl. Könikl. Akad. Amsterdam, Deel I, No. 1, 1892.
[2] Paschen: Ann. der Phys. (3), 53, p. 334, 1894.
[3] Aschkinass: Ann. der Phys. (3), 55, p. 406, 1895.

All have found water extremely opaque to infra-red radiation, so that the film had to be reduced to a few thousandths of a millimeter in order to be able to study it at all. In fig. 1 are given the absorption curves of water is found by Aschkinass. His values of the maxima are slightly greater than those found by others, but this is simply due to a fault in his calibration. The curves for the different thicknesses ($a = 0.05$;

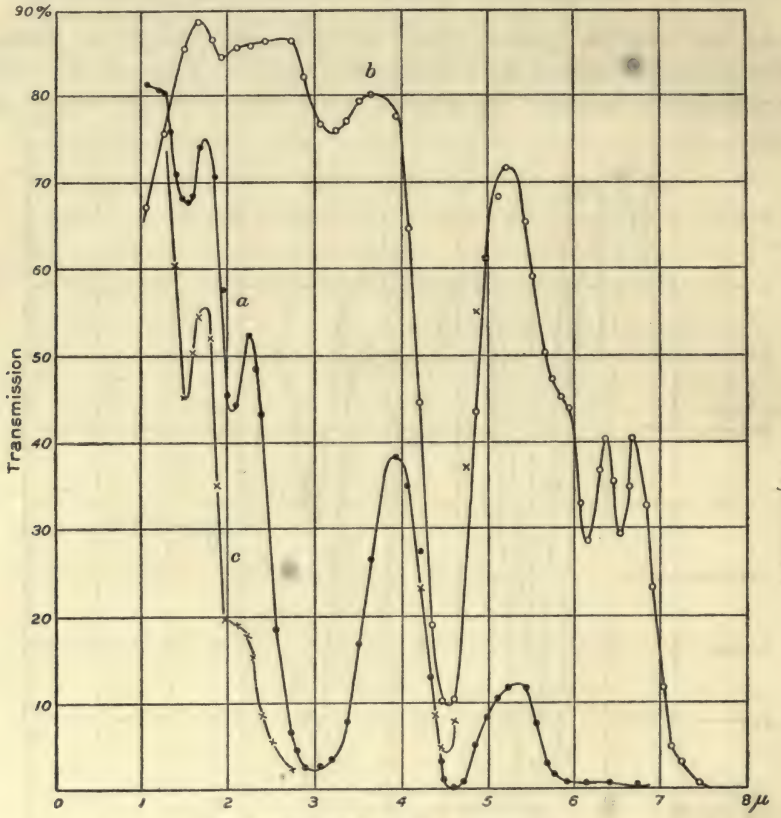

FIG. 2.—Selenite (*a* and *c*); Anhydrite (*b*).

$b = 0.01$ mm.) illustrate very well what we are to expect in the case of minerals containing several molecules of crystal water. For a very much thinner film (curve $c = 0.001$ mm.) by the writer[1] the absorption band at 4.75 μ has entirely disappeared.

SELENITE ($CaSO_4+2H_2O$); ANHYDRITE ($CaSO_4$).

(Figs. 2, 3, and 4. Selenite: Monoclinic, cleavage parallel to *b*; $t = 0.648$ mm. Anhydrite: Orthorhombic, cleavage piece parallel to *c*; $t = 0.656$ mm. From Stassfurt, Germany.)

Of all the minerals studied containing water of crystallization these two are the most conspicuous for demonstrating the effect of the presence

[1] Phys. Rev., 20, p. 257, 1905.

of H_2O. It would have been highly desirable to procure more minerals which occur in the hydrous and anhydrous state, but none were obtainable. The artificially dehydrated minerals, such as copper sulphate, were too opaque for examination after expelling all the water. The only exception is selenite, the various curves of which will now be considered. The anhydrite curve, *b*, is to be noticed first, from which it will be

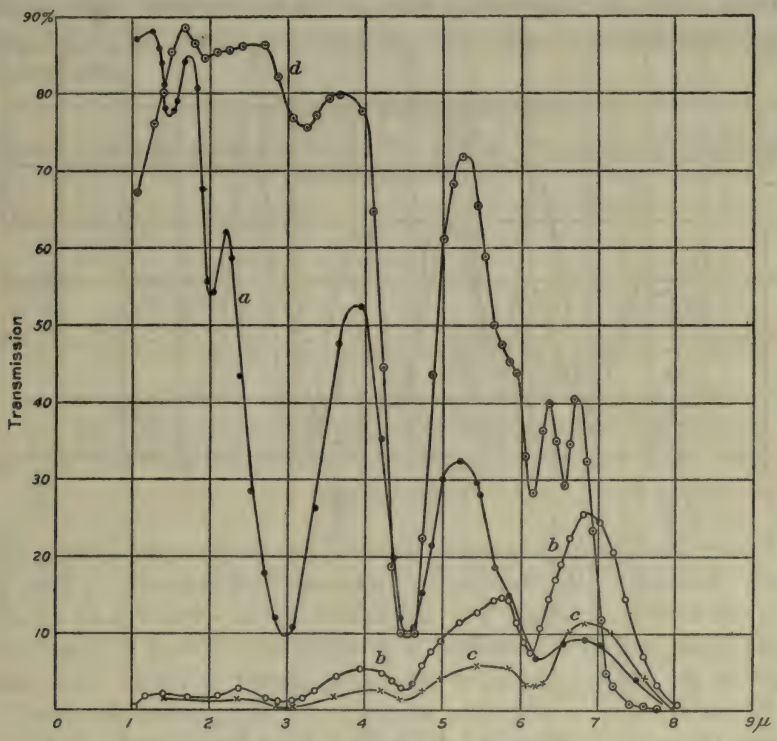

FIG. 3.—Anhydrite (*d*); Selenite.

observed that there are small bands at 1.9, 3.2, 5.7, 6.15, and 6.55 μ, and an enormous band at 4.55 μ, which will be shown later to be due to the SO_4 ion.

Turning to the selenite curve (*a*, fig. 2), it will be noticed that it is less transparent for the same thickness, 0.65 mm., and that in its general trend it is similar to the curve for water. All of its absorption bands coincide with water, with the exception of the 4.75 μ band, which is shifted to 4.6 μ. The shifting of this band is due to the SO_4 band at 4.5 μ, as was found on examining anhydrite.

The curve, *c*, for a thickness of 2.57 mm. is due to Königsberger (loc. cit.).

In fig. 3 is illustrated the effect of dehydrating the selenite. This was accomplished with difficulty on account of warping and shrinking of the plate, which necessitated dismounting the specimens for each heating. It was found necessary to clamp the specimen between two metal plates in order to prevent it from warping and breaking. Curve *a* gives the transmission of a clear piece having a thickness of 0.204 mm.; curve *b* shows the transmission after partial dehydration.

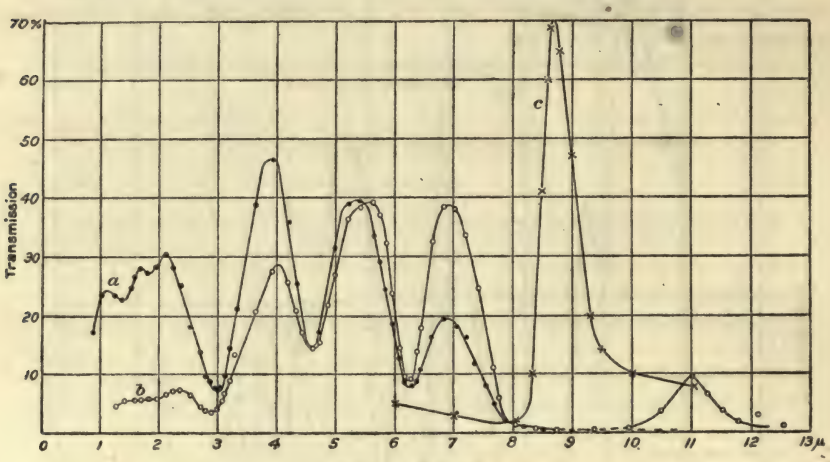

FIG. 4.—Selenite.

It is of considerable interest in showing the permanence of the 4.55 μ band. Beyond 6 μ the transparency increases and becomes 1.5 times as great as selenite at 6.9 μ. The dehydrated section, which is an opaque white mass, was then moistened with water and allowed to stand over night to dry and set, just as in the case of plaster of Paris. The result is shown in curve *c*, where the transparency at 6.9 μ has decreased to almost the original value found for the transparent crystal. It will of course be understood that the great opacity up to 5 μ for the dehydrated section is due to the lack of homogeneity introduced in expelling the water, which has the well-known property of scattering the radiation of short wave-lengths. At 7 μ the increase in absorption due to the presence of water can not be doubted.

In fig. 4 the transmission curves of a very much thinner partially dehydrated section are given. In curve *a* the section was subtransparent and in curve *b* it was translucent. The curves are given to show the increased transparency beyond the band of metallic reflection in the region of 9 μ.

Curve *c* shows the metallic reflection band found by Aschkinass,[1] and it will be noticed that the position of the maximum as found by him at 8.69 μ is shifted from that indicated by the present transmission curves. The same lack of coincidence of the maximum of the reflection band with the minimum in the transmission curve will be found in calcite and in mica. This is the first attempt to explore the region of transmission near a reflection band and the explanation to be offered later on for the discrepancy may not hold when more data have been accumulated.

QUARTZ (SiO_2); OPAL (SiO_2+xH_2O).

(Quartz: Cut perpendicular to axis; t = 1.30 mm. Opal: Massive, transparent; t = 0.12 mm. Fig. 5.)

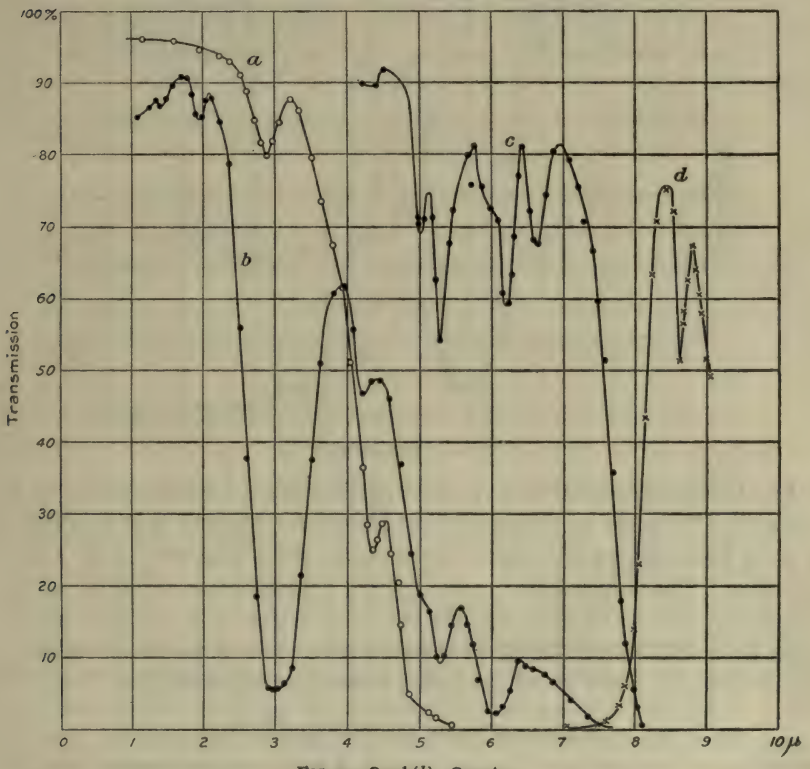

FIG. 5.—Opal (*b*); Quartz.

The specimen of quartz examined was made for polariscopic work and was perfectly clear. Its transmission curve (*a*, fig. 5) shows small bands at 2.9 μ and 4.35 μ. Curve *c*, which shows a series of bands at

[1] Aschkinass: Ann. der Phys. (4), 1, p. 42, 1900.

5.02, 5.3, 6, 6.26, and 6.65 μ, is due to Nichols,[1] who used a section 0.018 mm. thick. Unfortunately his curve begins in the slight band at 4.35 μ, so that there is no check upon its accuracy of location.

Königsberger[2] examined smoky quartz and found bands at 3.05 and 4.05 μ. Merritt,[3] using polarized light, found bands at 3 and 3.6 μ for the extraordinary ray, and bands at 2.9, 3.75, and 4.1 μ for the ordinary ray.

For amethyst, which is violet quartz, of which the color has been attributed to manganese, Königsberger found an absorption band at 3.1 μ. As a whole, different observers agree in locating a small band near 3 μ which will not interfere in considering water of crystallization.

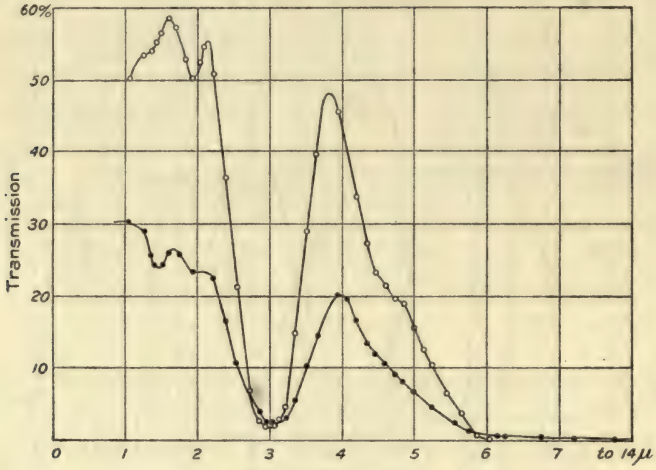

FIG. 6.—Heulandite.

Opal is quartz containing variable proportions of water, from 5 to 30 per cent. It shows no traces of crystallization. Neither is it considered a solid solution, for the water contained is not a function of the vapor pressure. The transmission curve of opal has the general outline of the curve for water and contains the bands of water at 1.5, 2, 3, and 6 μ, as well as the silicon bands at 4.2 and 5 μ. The 3 and 6 μ bands are the composite of the water and silicon bands in those regions.

HEULANDITE ($H_4CaAl_2Si_6O_{18}+3H_2O$).

(Section ground parallel to b; $t=0.20$ and 0.22 mm.; semi-transparent. Fig. 6.)

Heulandite belongs to a class of minerals called zeolites,[4] which are hydrated silicates of alumina, alkalies, and generally lime. To this class

[1] Nichols: Phys. Rev., 4, p. 297, 1896.
[2] Königsberger: Ann. der Phys. (3), 61, p. 687, 1897.
[3] Merritt: Ann. der Phys. (3), 55, p. 49, 1895.
[4] Miers: Mineralogy, p. 483.

belong heulandite, stilbite, analcite, natrolite, and scolecite, which are included in the present research.

In these minerals the water of crystallization is very loosely held. It is impossible to distinguish between water of constitution and water of crystallization. The water continues to be gradually expelled as the temperature is raised and may be replaced by other substances, such as NH_3, H_2S, or C_2H_5OH. The dehydrated crystals absorb definite quantities of these substances as a sponge absorbs water, the process being accompanied by the evolution of heat.

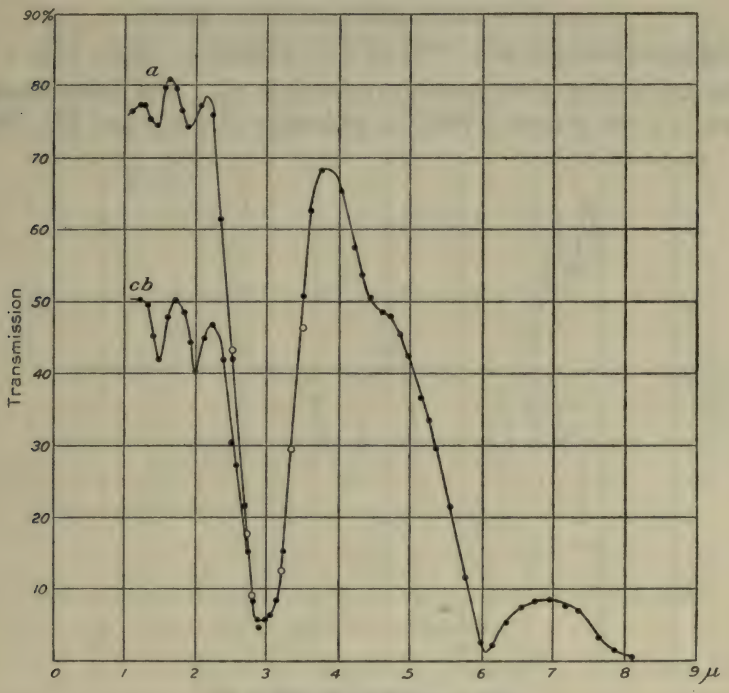

FIG. 7.—Stilbite (*a*); Potassium alum.

Since the per cent of water present varies continuously with the vapor pressure it is generally concluded that the water of the zeolites is not analogous to the water of crystallization of most hydrated salts, but resembles more nearly the intermixture which occurs in solid solutions.

In fig. 6 two curves of heulandite are given. The sections were about the same thickness, and the great difference in transparency is due to the fact that the crystals were of different homogeneity and transparency. The curves show the presence of the water bands at 1.5, 2,

3, and 4.75 μ, beyond which point the opacity becomes too great for further exploration. The crystals obtainable were small, so that the section was not quite long enough to cover the whole slit.

STILBITE ($CaAl_2Si_6O_{16}+6H_2O$).

(Transparent section cut perpendicular to optic axis. $t=0.11$. Curve *a*, fig. 7.)

The stilbite curve is to be noticed for its great transparency with all the water bands superposed. There do not appear to be any important bands belonging to the mineral itself.

POTASSIUM ALUM ($K_2SO_4Al_2(SO_4)_3+24H_2O$).

(Cut perpendicular to axis. $t=0.085$ mm.; transparent. Curve *b*, fig. 7.)

The exploration of the spectrum extends to 3 μ. The water bands at 1.5 and 2 μ are present. With 24 molecules of water and SO_4 bands

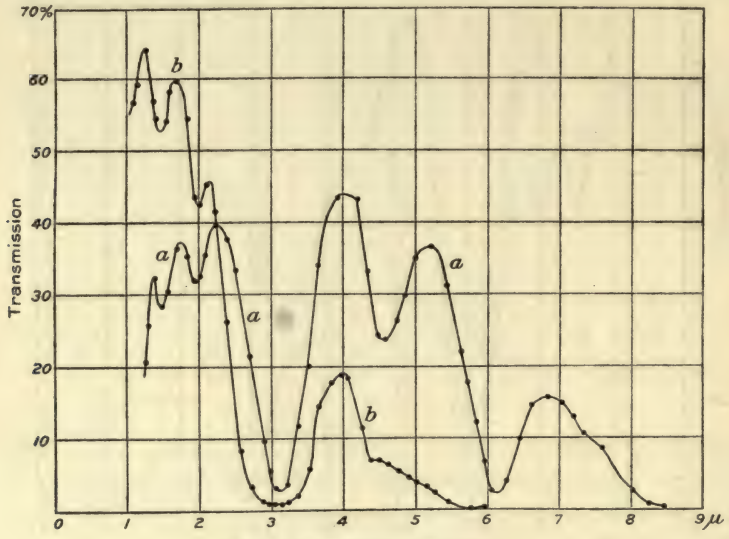

FIG. 8.—Natrolite (*a*); Scolecite.

at 455 μ, to be mentioned later, it would not be possible to penetrate beyond 3 μ, unless a thinner section could be made.

NATROLITE ($Na_2Al_2Si_3O_{10}+2H_2O$).

(Orthorhombic section ground parallel to *m*; subtranslucent; $t=0.11$ mm. Curve *a*, fig. 8.)

The specimen from which this section was cut was a tuft of acicular crystals. The section was made from the more massive part, and was almost opaque for the thickness used. The curve (*a*) in fig. 8 shows the water bands in their usual positions and proper intensities.

SCOLECITE ($CaAl_2Si_3O_{10}+3H_2O$).

(Monoclinic section split parallel to *m*; perfectly transparent; $t=0.565$ mm. Curve *b*, fig. 8.)

This mineral differs from the preceding in being a lime zeolite, and in having one more molecule of water. Its greater homogeneity makes it more transparent in the region of the short wave-lengths. It has the general outline and the absorption bands of the water curve up to 5 μ, where it is completely opaque. The 3 μ band is evidently complex. Prof. S. L. Penfield kindly presented this specimen.

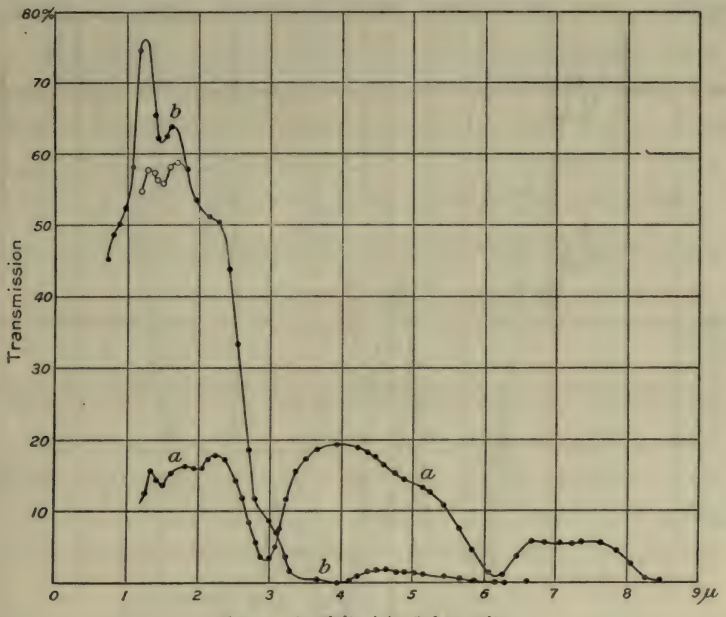

FIG. 9.—Analcite (*a*); Colemanite.

ANALCITE ($Na_2Al_2Si_4O_{12}+2H_2O$).

(Cut perpendicular to optic axis; subtransparent; $t=0.11$ mm. Fig. 9.)

This specimen, made by Steeg & Reuter, was small and broken in shipping, so that by placing two pieces end to end the spectrometer slit was not quite covered. Nevertheless it shows a transparency farther into the infra-red than is usual. As a whole, however, it is very opaque (curve *a*, fig. 9), and the water bands at 1.5, 2, and 4.7 μ are quite obliterated. There seem to be no other than water bands.

COLEMANITE ($Ca_2B_6O_{11}+5H_2O$).

(Cut parallel to *b*; transparent; $t=0.268$ mm. Curve *b*, fig. 9.)

This mineral is obtainable in large transparent crystals. Nevertheless, it is unusually opaque to infra-red radiation, so that very little

energy is transmitted beyond 3 μ; even the water bands at 1.5, 2 and 3 are almost obliterated. As the examination proceeds it will be noticed that this opacity appears to be a property of the borates.

CALCIUM CHLORIDE ($CaCl_2+6H_2O$).

(Film melted between rock-salt plates. $t=0.1$ mm. Fig. 10.)

This compound comes in large hexagonal crystals. A specimen was melted between two plates of rock salt, and stood over P_2O_5 for several days, until the edges became white from dehydration. The substance

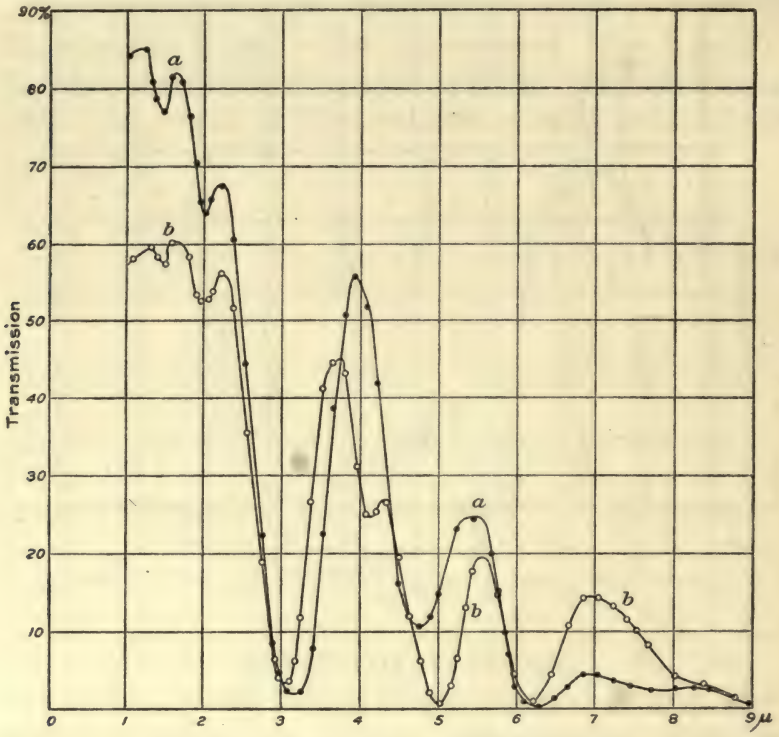

FIG. 10.—Calcium chloride (*a*); Potassium ferrocyanide.

recrystallized in the meantime and when examined showed the water bands in their usual position and intensities except the 3 μ band, which is shifted to 3.2 μ.

POTASSIUM FERROCYANIDE ($K_4Fe(CN)_6+3H_2O$).

(Section split parallel to *c*; transparent; $t=0.3$ mm. Fig. 10.)

The water is so easily expelled from this mineral that the heater had to be used on 70 volts. The transmission curve shows the water bands

at 1.5, 2, and 3 μ, while the next two bands are shifted to 5 and 6.2 μ respectively. Porter,[1] by means of "reststrahlen," located a band at 4.84 μ.

APOPHYLLITE ($H_7KCa_4(SiO_3)_8+4\frac{1}{2}H_2O$).

(Section cut parallel to *c*; transparent; $t=0.11$ mm. Fig. 11.)

This mineral is entirely opaque beyond 3 μ up to 8 μ, where there is slight transparency. The water bands at 1.5 and 2 μ are almost obliterated.

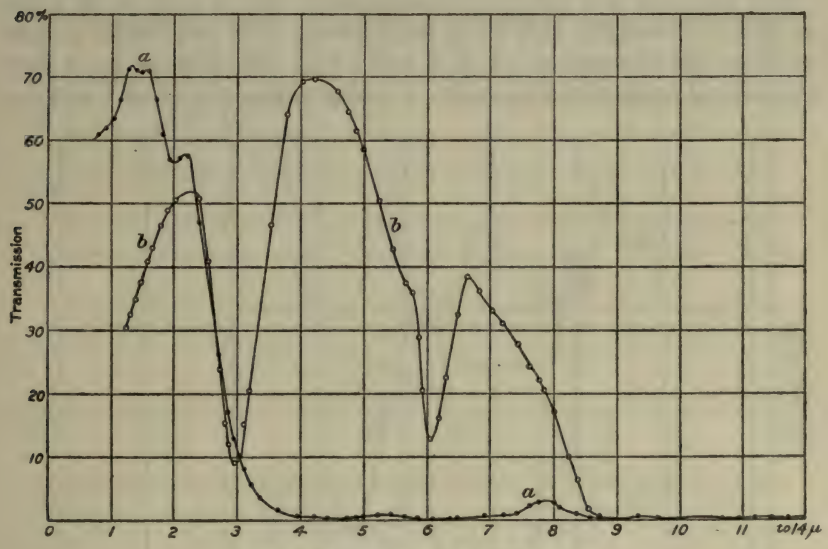

FIG. 11.—Apophyllite (*a*); Deweylite (*b*).

DEWEYLITE ($H_4Mg_4(SiO_4)_3+4H_2O$).

(Massive; whitish color; subtranslucent in section 0.08 mm. thick. From New Rochelle, New York. Fig. 11.)

In the curve, *b*, for this mineral the small absorption bands are obliterated but the bands at 3 μ and 6 μ are very strong, which would make it appear that the water is present in the form of water of crystallization.

THOMSENOLITE ($NaCAlF_6+H_2O$).

(Monoclinic; cleavage parallel to *c*; transparent; $t=0.75$ mm. From Ivigtut, Greenland. Curve *a*, fig. 12.)

This mineral was obtained as a mass of small crystals, from which one was obtained having an area of about 4 by 5 mm. This crystal

[1] Porter: Ap. Jr., 22, p. 229, 1906.

was split into two inclined prisms, which, when placed end to end, made a tight joint. The transmission curve, *a*, shows all the absorption bands of water in their proper intensities. A new band occurs at 2.6 μ which widens the one at 3 μ but does not displace it. The specimen suddenly becomes opaque at 6 μ.

GISMONDITE ($H_4(Na_2Ca)Al_2Si_6O_{18}+4H_2O$).

(Stalactitic mass; subtranslucent; $t=0.245$ mm. From County Antrim, Ireland. Fig. 12.)

This specimen was not very homogeneous, but, in spite of its great complexity chemically, it is fairly transparent. The only bands present are those due to water at 1.5, 2, 3, and 4.7 μ. The band at 3 μ is very wide, which suggests the presence of others, perhaps of silicon, at 2.9 μ.

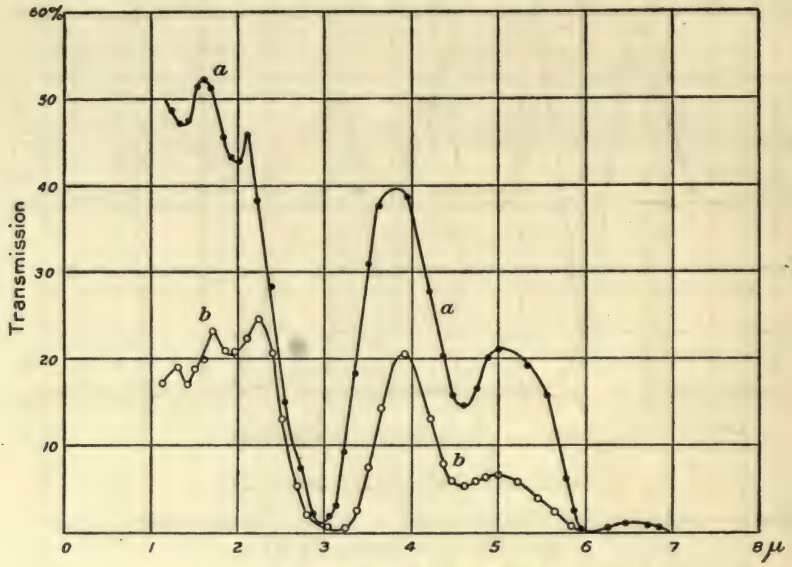

FIG. 12.—Thomsenolite (*a*); Gismondite.

BLÖDITE ($MgSO_4NaSO_4+4H_2O$).

(Cut perpendicular to axis; $t=0.10$ mm. Curve *a*, fig. 13.)

This mineral shows all the water bands, the one at 2 μ being conspicuous for its sharpness. The band at 4.6 is composite, due to the SO_4 band at 4.55 μ, as will be shown in discussing the sulphates, while the 3 μ band is also complex.

THAUMASITE ($CaSiO_3CaCO_3CaSO_4+15H_2O$).

(Cut perpendicular to axis; transparent; $t=0.125$ mm. Fig. 13.)

This mineral is too opaque for heat rays to be considered in demonstrating the presence of water of crystallization. The water bands at

1.5 and 2 μ are well defined, considering the great opacity of the substance.

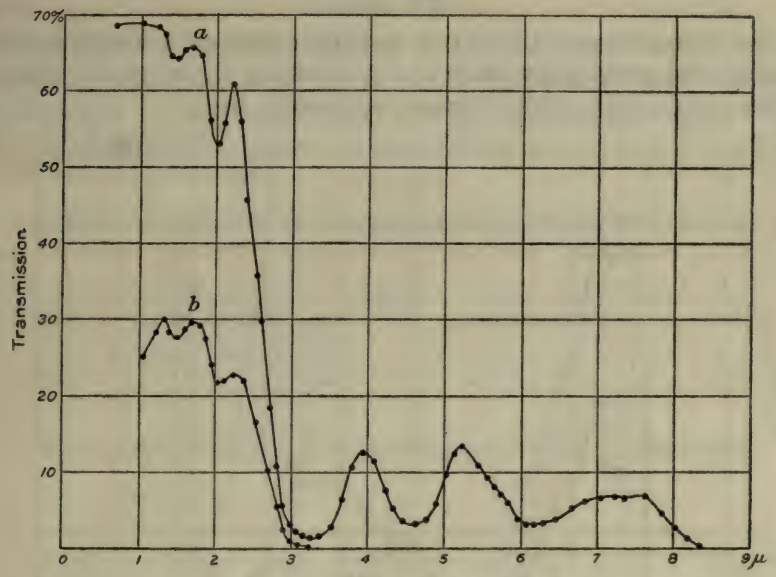

FIG. 13.—Blödite (*a*); Thaumasite (*b*).

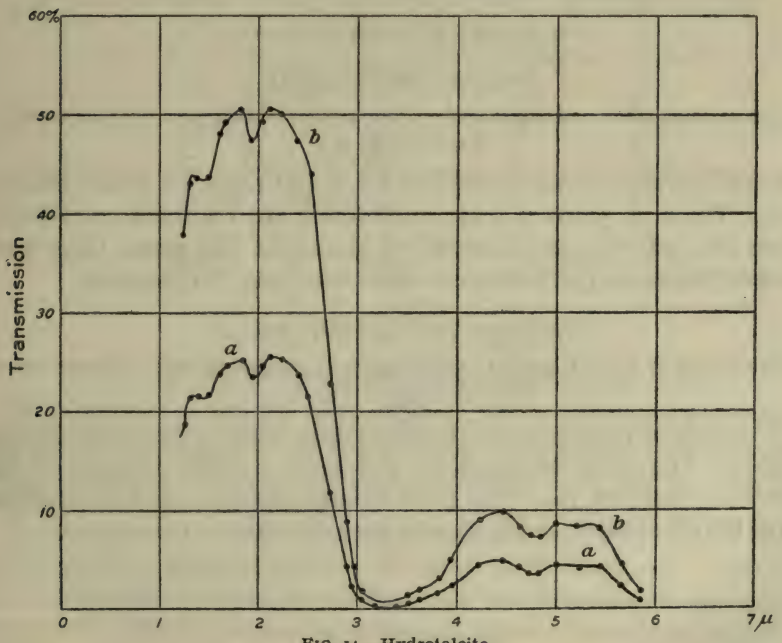

FIG. 14.—Hydrotalcite.

HYDROTALCITE ($Mg_3Al(OH)_8+3H_2O$).

(From Vernon, New York. Lamellar; massive; subtranslucent; $t=0.04$ mm. Fig. 14.)

The hydroxide group (OH), to be noticed later on, confuses matters at 3 μ. The other water bands at 1.5, 2, and 4.75 μ are visible in spite of the great opacity, which becomes complete at 6 μ.

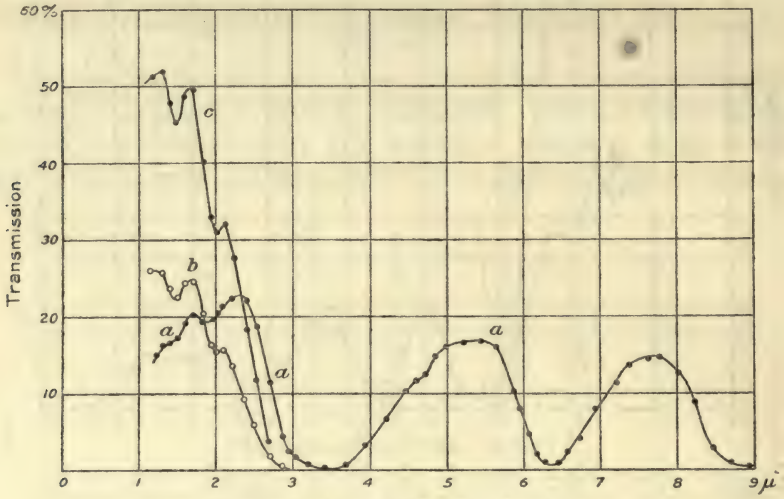

FIG. 15.—Varicite (*a*); Wavellite (*b* and *c*).

VARICITE ($AlPO_4+2H_2O$).

(Massive; blue color; subtranslucent in thin section of 0.03 mm. From Lewiston, Utah. Fig. 15.)

In this mineral the water bands at 1.5, 2, and 4.75 μ are almost obliterated. Those at 3 and 6 μ are shifted and are no doubt composites. From this and other minerals studied, having the PO_4 group, there is no marked evidence of an absorption band belonging to this group.

WAVELLITE ($Al(OH)_3(PO_4)_2+5H_2O$).

(Crystallized in rays of needles; section ground parallel to rays; subtranslucent. From Arkansas. Fig. 15.)

The lack of homogeneity of the crystals renders this mineral very opaque. The water bands at 1.5 and 2 μ are visible, in spite of the complete opacity at 3 μ. This great opacity appears to be a characteristic of the phosphates, as has already been observed in the borates.

VIVIANITE ($Fe_3(PO_4)_2+8H_2O$).

(Monoclinic; section ground parallel to *b;* bluish color; translucent; $t=0.11$ and 0.25 mm. Fig. 16.)

This section is practically opaque beyond 3 μ. The water bands at 1.5 and 2 μ are visible, although slightly shifted, which is due to general transparency of the mineral. This is well illustrated in curve *c*, which is curve *b* magnified 5 times. I am indebted to the late Prof. S. L. Penfield for this mineral.

FIG. 16.—Vivianite.

MELLITE ($Al_2C_{12}O_{12}+18H_2O$). (Fig. 17.)

This mineral occurs as waxy crystals of variable transparency in European coal measures. It was selected on account of its carbon, and also because of the large number of molecules of water, which is expelled at a low temperature.

In fig. 17, curve *a*, is given the transmission curve of a mineral from Steeg and Reuter, purporting to be mellite or "honeystone," $t=0.125$ mm. It was the most flagrant exception to the rule that minerals having water of crystallization are very opaque and have absorption bands in

common with water. Evidently this needed further investigation; and this was done with minerals purchased from various dealers, care being taken to obtain them from different localities. Curves *b* and *c* give the transmission for transparent yellow crystals, t=0.7 and 0.15 mm. respectively, which came from Arten, Thuringia. Curve *d* is the transmission for a grayish-white translucent crystal, ground to 0.12 mm. in thickness, from Mallonka, Austria. Curve *e* is for a white transparent crystal, 0.06 mm. in thickness, from Tula, Russia. In all these curves it will be noticed there is no energy transmitted beyond

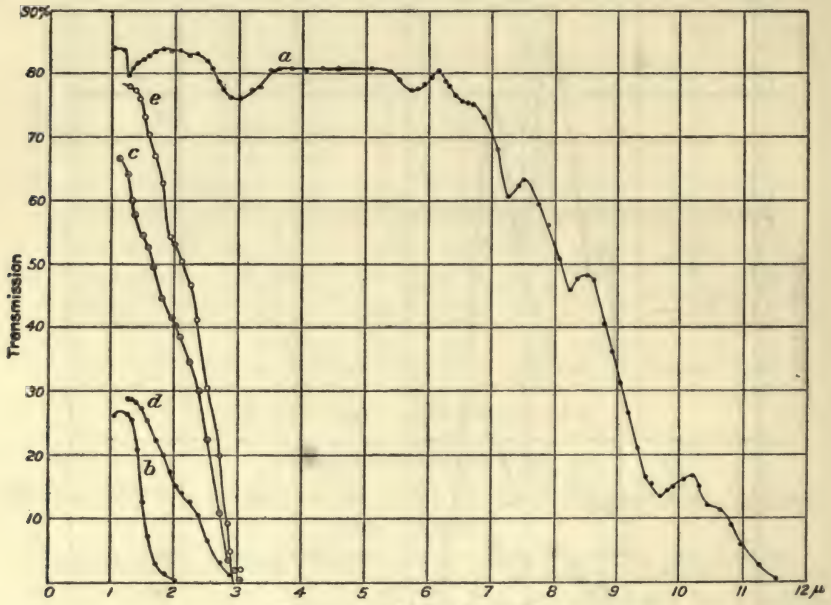

FIG. 17.—Cassiterite (*a*); Mellite.

3 μ, while from the very nature of the transmission curves the 1.5 band is invisible and the 2 μ band is almost obliterated. As a whole the theory that, in crystal-water, the bonding is the same as in ordinary water has also been confirmed with mellite. A letter of inquiry to Steeg and Reuter in regard to the sample sent us revealed the fact that cassiterite (SnO_2) was accidentally substituted for mellite. The fact that it was possible to detect the error would indicate that the method of analysis is trustworthy, and in that respect it is fortunate that the substitution occurred.

d-FRUCTOSE ($C_6H_{12}O_6$).

(t = 0.1 mm. Fig. 18.)

The sugars are complex carbohydrates, the constitution of which is not well known. They are rich in hydroxyl groups similar to the alcohols, and hence one would expect to find a band at 3 μ. We would also expect a band at 3.43 μ due to CH_2 or CH_3 groups, so that as a whole the curve will be complex at 3 μ. The water bands at 1.5, 2,

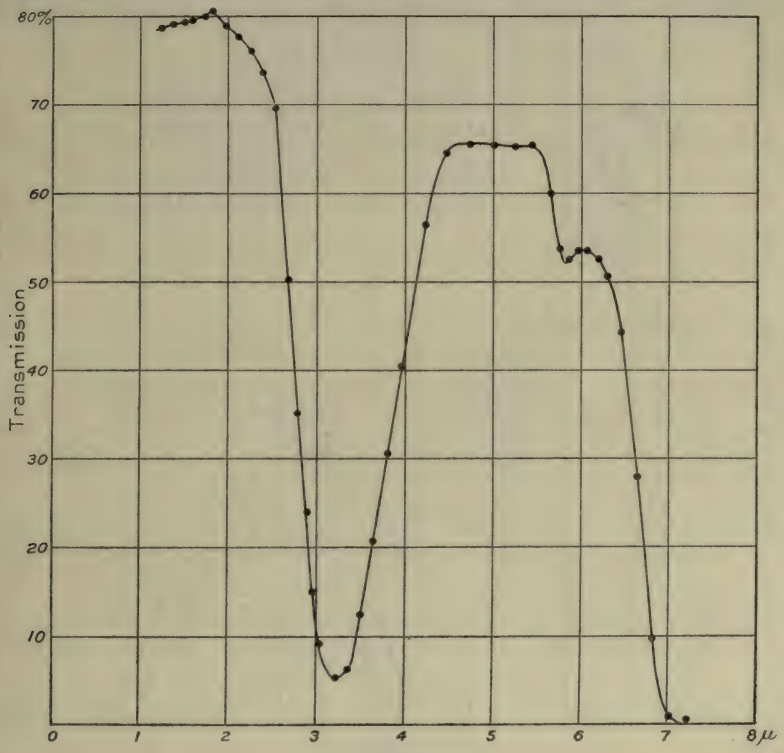

FIG. 18.—*d*-Fructose.

and 4.5 μ should appear in those compounds containing water of crystallization. The region from 4 to 6 μ ought to be one of great transparency if previous results hold. It is a property of sugars that they decompose and give off water when heated above the melting-point.

In *d*-fructose ($C_6H_{12}O_6$) the constitutional formula is written $CH_2OH(CHOH)_3COCH_2OH$. The curve (fig. 18) shows *no* absorption in the region of the water bands. There is a large band at 3.25 μ and a small one at 5.85, while beyond 7 μ there is complete opacity.

Fructose belongs to the anhydrous group of compounds, but is considered here in order to show the great contrast between it and other sugars having water of crystallization.

d-Glucose (Dextrose) ($C_6H_{12}O_6+H_2O$).

($t=0.14$ and 0.18 mm. Fig. 19.)

This compound differs from the preceding in having one molecule of water of crystallization. The region of 3 to 4 μ is very complex and indeterminate, but the water bands appear at 1.5, 4.75 and 6 μ, the

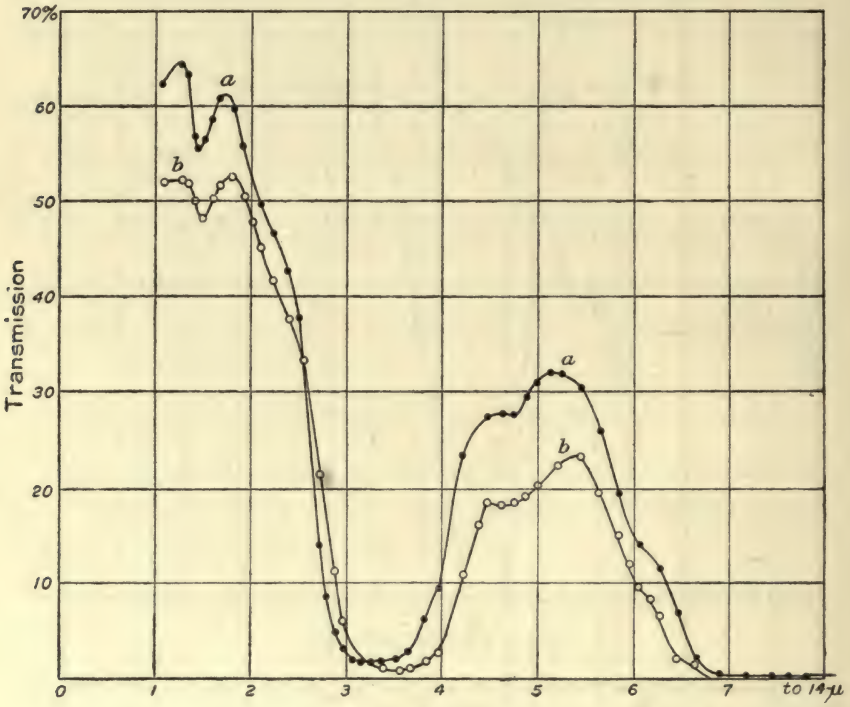

Fig. 19.—Dextrose.

latter being quite indistinct. A sample was heated at 110° for four hours which is supposed to render it anhydrous. After standing over P_2O_5 for several days, several crystals had formed in the glassy mass. These were melted between plates of rock salt. Curve *b* shows, however, that the water bands still remain, and from the fact that the amorphous material could not be entirely removed from the crystals it is quite probable that there was still some of the hydrous material present.

CANE SUGAR ($C_{12}H_{22}O_{11}$).

(Melted between rock salt; $t = 0.1$. Figs. 20 and 20a.)

In fig. 20 are given a series of curves for different samples of cane sugar, which is supposed not to contain water of crystallization. It is one of the most conspicuous exceptions to the rule, if it really be anhydrous. Curve *a* represents the transmission for barley sugar, which is the name given to cane sugar after it has been melted, when it becomes an amorphous mass. Curve *b* is another sample, partially dehydrated and decomposed, called "caramel." It was light brown. Curve *c* is for

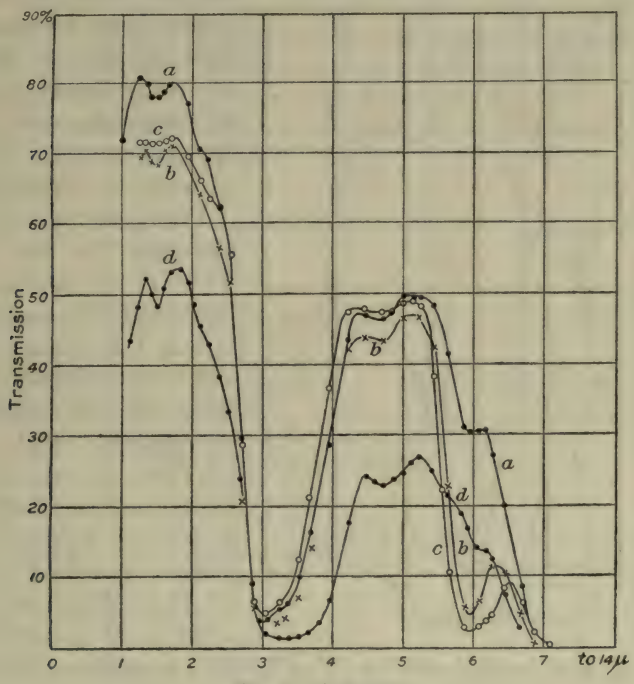

FIG. 20.—Cane sugar.

a dark-brown caramel made by driving off some 15 per cent of the water. In this sample it will be noticed that the 1.5 and 4.75 μ water bands have quite disappeared, which is to be expected.

Curve *d* shows the transmission through a film ($t = 0.2$ mm.) of chemically pure sugar. It was an amorphous solid melted between two plates of rock salt. It was originally crystallized from alcohol and, hence, was free from water. The amorphous film was colorless, showing that there was no decomposition in melting. Nevertheless the water bands at 1.5, 2 and 4.75 μ are present.

Curve *f*, fig. 20*a*, is for an amorphous film of beet sugar, which also shows the 1.5 μ band. Curves *e* and *h* are for two large, clear crystals of rock candy, respectively 2 and 1.7 mm. in thickness, in which the 1.5 μ band is unusually strong, which would indicate that there was no decomposition in melting the other films. An analysis by Dr. J. C. Blake showed that the rock candy contained 99.81 per cent pure sugar, while the water content was about 0.05 per cent. Now, it has never before been suspected that cane sugar has water of crystallization, and the present disagreement with the results of chemists who have made a life-long study of sugars in general must be considered with caution. A comparison with lactose, maltose, and dextrose would indicate the presence of a molecule of water of crystallization.

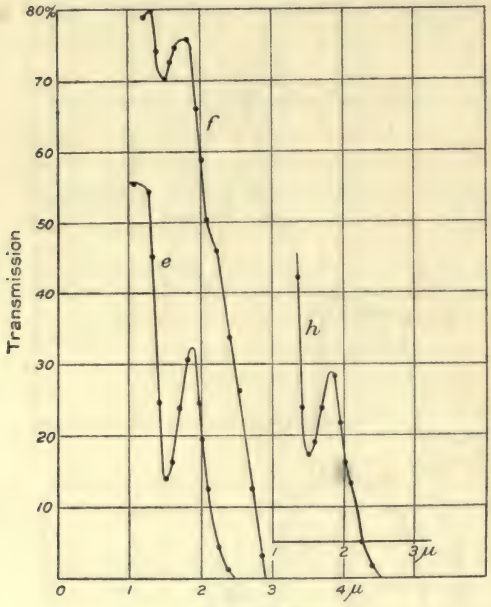

FIG. 20*a*.—Cane sugar.

There may be other explanations for this exception. It has already been noted that the sugars are rich in OH groups, which will confuse matters at 3 μ where the OH radical has a characteristic band, so that the effect of water must be based upon the small bands at 1.5 and 4.75 μ. In the present work on mannite ($C_6H_8(OH)_6$) and in previous work[1] on ethyl alcohol (C_2H_5OH) and myricyl alcohol ($C_{80}H_{61}OH$), as well as on glycerin and on phenols, there is no indication of absorption bands at 1.5, 2, 4.75, and 6 μ, so that their presence in the cane-sugar spectrum can hardly be attributed to the OH group. In Puccianti's curves[2] the alcohols show depressions at 1.5 μ, but they are not very sharp, although he used a larger dispersion and a thicker cell. As a whole, the question is in an unsettled state with the results obtained by the method of absorption spectra indicating the presence of a molecule of water of crystallization in cane sugar which has heretofore been considered to be composed entirely of water of constitution.

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[1] Investigations of Infra-red spectra, Washington, 1905.

[2] Puccianti: Nuovo Cimento, II, p. 241, 1900.

MALTOSE ($C_{12}H_{22}O_{11}+H_2O$); LACTOSE ($C_{12}H_{22}O_{11}+H_2O$). (Fig. 21.)

These two compounds were melted between plates of rock salt, dried over P_2O_5 and the edges sealed with Kohtinsky cement. The thickness

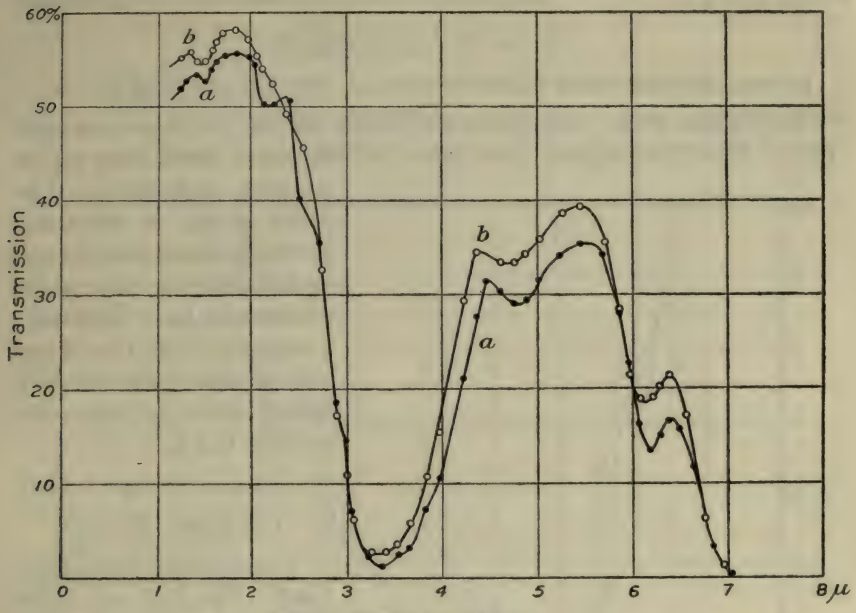

FIG. 21.—Maltose (*a*); Lactose.

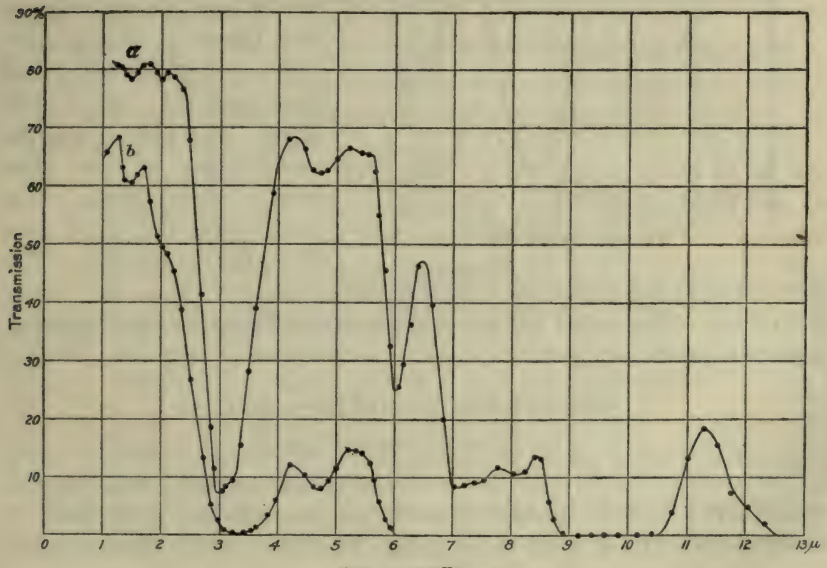

FIG. 22.—Raffinose.

of the films was about 0.1 mm., and in the case of lactose the color was slightly tinged, due to decomposition. The water bands are present as noted elsewhere. The region from 3 to 4 μ is complex, with the maximum at 3.4 μ.

RAFFINOSE ($C_{18}H_{32}O_{16}+5H_2O$).

(Amorphous solid melted between rock salt; $t=0.2$ and 0.05 mm. Fig. 22.)

This sugar melts very easily and forms perfectly transparent solid films. The transmission curve shows all the water bands, viz, 1.5, 2, 3, 4.75, and 6.05 μ. The band at 3 μ is quite distinctly resolved into the second component lying in the region of 3.3 μ. The transparent region at 11 μ is just the reverse of the alcohols, which have an absorption band at 11.3 μ.

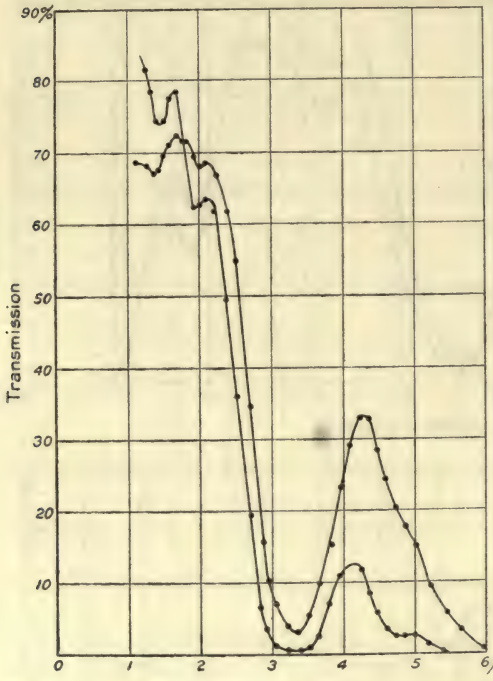

FIG. 23.—Gum arabic.

GUM ARABIC ($2C_6H_{10}O_5+H_2O$).

($t=0.1805$. Fig. 23.)

Two samples were examined. The first was a film of the gum dissolved in water and placed between two plates of thin microscope cover-glass, which was kept over P_2O_5 for several days. The second was the combination of two films which were spread over cover-glass and dried over P_2O_5 for several days. The films cracked and peeled off, so that it was necessary to place two facing each other. The water bands are of course visible, while the region at 3.5 μ is complex.

ROCHELLE SALT ($C_4H_4O_6KNa+4H_2O$).

($t=1.27$ and 0.1 mm. Fig. 24.)

Curve *a* shows the transmission through a transparent crystal section, while curve *b* is for a solid film melted between two thin plates of cover-glass. In the latter case the film was flaky, which decreased the

transparency. The crystal section was examined with difficulty because of its low melting-point. Curve *c* shows the band at 4.75 μ magnified 10 times. The water bands at 1.5, 2, and 4.75 μ are very apparent, while the one at 3 μ is obliterated, as with the sugars.

BRUCINE ($C_{23}H_{26}N_2O_4+4H_2O$).

(Thickness: $a=0.05$; $b=1.15$ mm; $c=0.15$ mm. Fig. 25.)

Brucine belongs to the alkaloids, which have a complicated and unknown structure. As will be noticed from the curves it is very

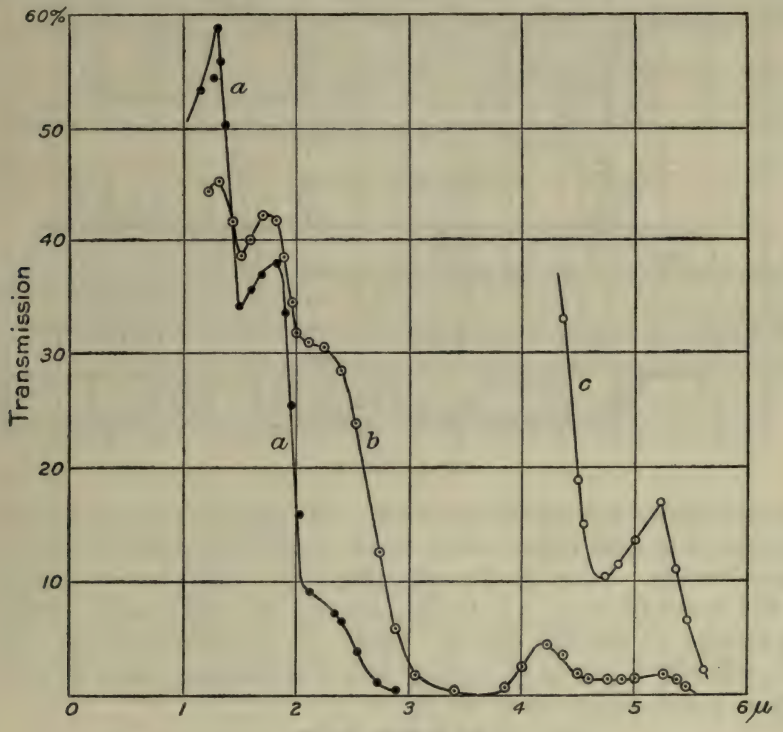

FIG. 24.—Rochelle salt.

transparent to contain 4 molecules of crystal water. The 6 μ band is the only one that is conspicuous, while the strong one at 3 μ is entirely absent. The water is easily expelled at a low temperature. Curve *b* is for a thick layer of amorphous material melted *on* a plate of rock salt. It shows the general carbohydrate band at 1.7 μ, and the 3.43 μ band characteristic of compounds rich in CH_2 or CH_3 groups. For curve *a* the film was made by placing the solid powder between two plates of rock salt, which were heated on a metal plate, and as soon as

melting began, the rock salt, containing the film, was removed. In the same manner the film for curve *c* was obtained, but here it was not permitted to melt entirely, so that the film was only semi-translucent. Nevertheless, it does not show the water bands at 1.5 and 3 μ. It is difficult to conceive how all the water was expelled in these two cases. Curve *d* is curve *c* magnified 10 times at 3 μ.

Out of a list of 32 substances examined containing water, generally in the form of water of crystallization, this is the first exception to the

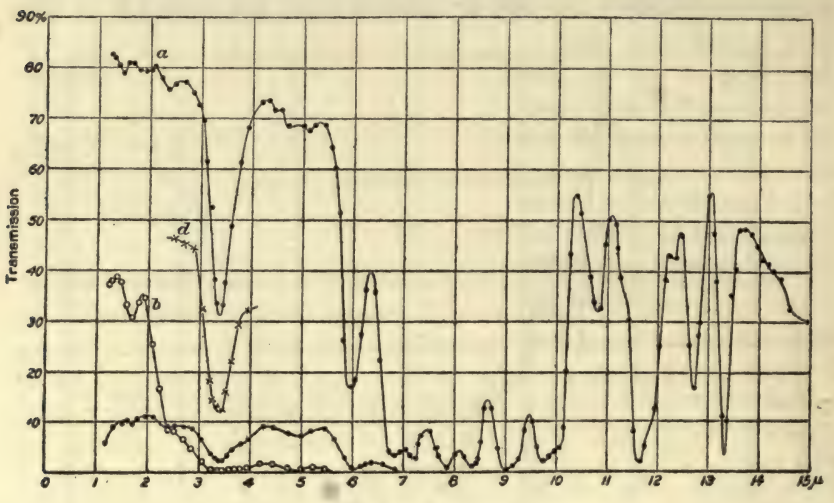

FIG. 25.—Brucine.

rule tentatively assumed in this work. The second exception thus far considered is cane sugar, which is not supposed to contain water of crystallization. In fig. 40 Kieserite ($MgSO_4+2H_2O$) is to be noticed. It has water bands at 1.5, 3, 4.55, and 6 μ, the latter being complex on account of the SO_4 groups. In fig. 42, cadmium sulphate ($3CdSO_4+8H_2O$) is also to be noticed, since it contains the water bands at 1.5, 2, 3, and 4.6 μ.

GROUP II: MINERALS CONTAINING WATER OF CONSTITUTION.

The first part of this group contains minerals in which the oxygen and hydrogen are present in the form of the univalent hydroxyl radical, OH, and are known as hydroxides. The hydroxides when heated also yield water, but it is a characteristic that they must be strongly heated before they are decomposed. From previous work, already noticed, we would expect an absorption band at 3 μ for hydroxides.

MANGANITE, MnO(OH).

(Orthorhombic; ground parallel to *m*; opaque; $t = 0.08$ mm. Fig. 26.)

As will be noticed in curve *a* of fig. 26, manganite has no sharp bands throughout the whole region to 9 μ. There is a light indication of a band at 3 μ and another at 6.2 μ.

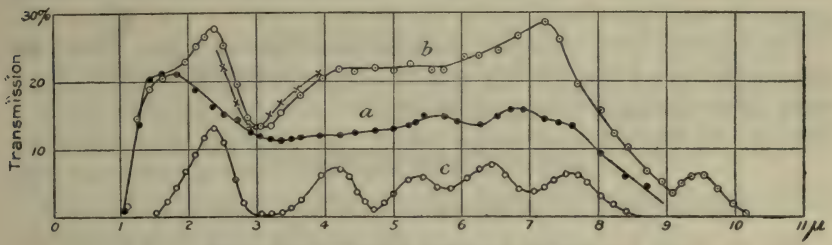

FIG. 26.—Manganite (*a*); Göthite (*b*); Bauxite (*c*).

GÖTHITE, FeO(OH).

(Section ground parallel to *b*; $t = 0.15$ mm. Curve *b*, fig. 26.)

The appearance of this mineral is opaque black, metallic luster, and as a whole would not impress one as being quite transparent to 9 μ. It transmits about 20 per cent of the energy throughout this whole region, which is in marked contrast with the almost complete opacity of iron. The 3 μ band is well marked, while a second one occurs at 9 μ. This specimen was kindly presented by the late Prof. S. L. Penfield.

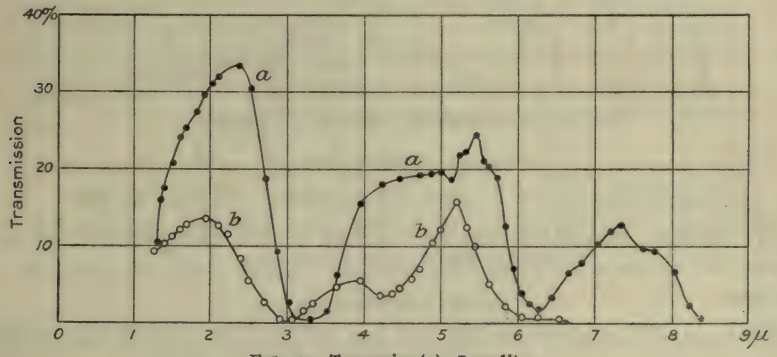

FIG. 27.—Turquoise (*a*); Lazulite.

BAUXITE ($Al_2O(OH)_4$).

(Chocolate-brown color; $t = 0.11$ mm. Curve *c*, fig. 26.)

In this mineral the 3 μ band is wide and complex. There are other bands at 4.7, 5.8, and 7 μ.

TURQUOISE ($AlPO_4Al(OH)_2+H_2O$).

(Massive, light green; subtranslucent in section of 0.1 mm. Curve *a*, fig. 27.)

This mineral is supposed to contain a molecule of water, although Miers writes the formula without it. The OH groups will cause a band at 3 μ, and in general the substance is opaque so that it is difficult to decide that question.

The region at 3 μ is complex, with the maximum at 3.3 μ. There are other bands at 5.1, 5.3, 5.6, 6.3, and 7.6 μ, all of which are small. There seem to be no bands belonging to PO_4.

LAZULITE, $(MgFe)Al_2(OH)_2(PO)_2$.

(Massive; blue by transmission; $t=0.19$ mm. Curve *b*, fig. 27.)

The 3 μ band is prominent, while a new band appears at 4.3 μ.

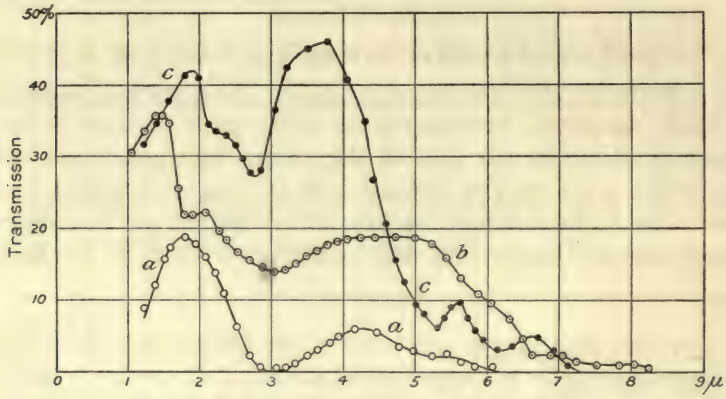

FIG. 28.—Hydrargillite (*a*); Diaspore (*b*); Datolite (*c*).

HYDRARGILLITE ($Al(OH)_3$).

(Stalactitic mass; $t=0.2$ mm.; subtranslucent. Curve *a*, fig. 28.)

The section obtainable was only about 6 mm. long, which did not cover the entire slit; hence the capacity is not quite so great as it appears.

There is only one large band, at 3 μ, which is no doubt due to the OH radicals.

DIASPORE, $AlO(OH)$.

(Cleavage piece parallel to *b*; $t=0.18$. Curve *b*, fig. 28.)

The specimen was transparent, with a few patches that were translucent. The specimen came from Professor Penfield. The band at 3 μ is wider and not so well defined as in the preceding. There are smaller absorption bands at 1.9, 5.8, and 6.7 μ.

DATOLITE ($Ca(BOH)SiO_4$).

(Section ground to 0.23 mm. Curve *c*, fig. 28.)

In this curve the OH band at 3 μ is shifted to 2.8 μ. The other bands present are at 2, 3, 5.3, and 6.3 μ. Although the specimen was full of cracks, it is rather transparent for a boro-silicate.

AZURITE ($2CuCO_3.Cu(OH)_2$).

(Translucent; section parallel to *c*; $t = 0.35$ mm. thick. Fig. 29.)

The section was ground from a group of crystals all of which were apparently piled parallel to *c*. There are absorption bands at 2.5, 3.05, 3.58, and 4.05 μ and complete opacity beyond 5.5 μ.

The 3.05 μ band is shifted slightly from the position common to substances containing OH groups.

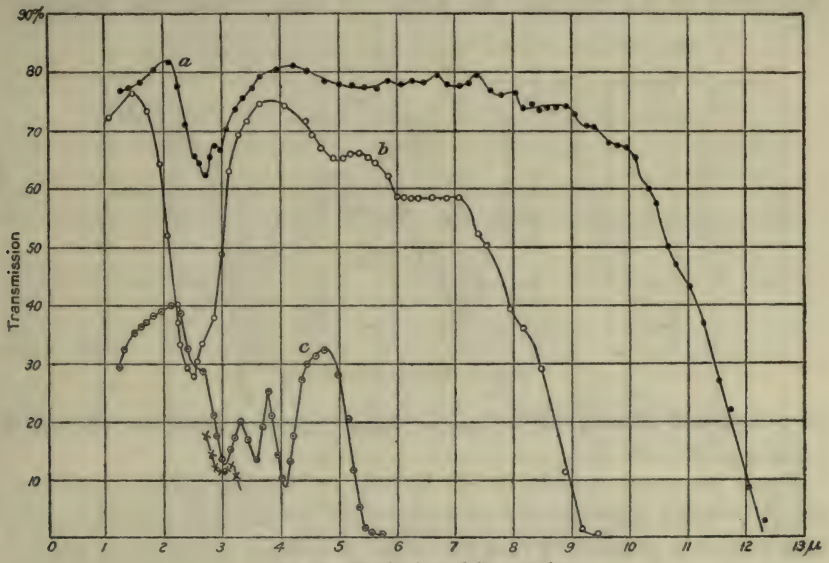

FIG. 29.—Brucite (*a* and *b*); Azurite.

BRUCITE ($Mg(OH)_2$).

(From Woods Mine, Lancaster County, Pennsylvania. Foliated; massive; lamina parallel to *c*; $t = 0.05$ and $t = 0.19$ mm. Fig. 29.)

As mentioned elsewhere, the fact that brucite did not show an absorption band at 3 μ, which is the maximum of the hydroxyl group in a series of organic compounds previously studied, made a reëxamination highly desirable. Of course, as will be noticed in curve *b*, by straining matters one might have concluded that the band at 2.5 μ, which evidently is complex, containing the 3 μ band. In the present

examination the cleavage section was perfectly transparent and much thinner than the previous one. Furthermore, the dispersion is greater, so that as a whole this large band is resolved into three components with maxima at 2.5, 2.7, and 3 μ. Beyond this region there are no marked bands, while beyond 12 μ there is complete opacity. The curve shows depressions at 5, 7, 7.7, 8.2, 9.7, and 10.8 μ, but as a whole the curve is conspicuous for the complete absence of sharp absorption bands, except at 2.7 μ, and is similar to glass and the micas.

PORTLAND CEMENT.

(t = 0.17 mm. Fig. 30.)

The specimen examined was ground thin from a piece made for tensile-strength tests, and, in making it, was mixed with 21 per cent of water. The chemical constitution of Portland cement is unknown. According to Le Chatlier[1] the action of water causes the formation

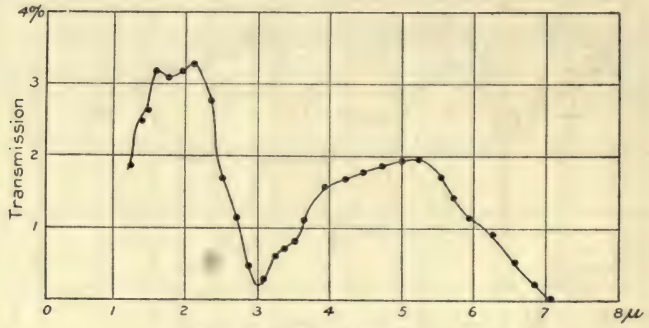

FIG. 30.—Portland cement.

of a hydrous silicate ($2(SiO_2CaO)5H_2O$) and a hydrous aluminate ($Al_2O_3.4CaO.12H_2O$).

From the present curve it will be noticed that the substance is very opaque, with a large absorption band at 3 μ, which would seem to indicate hydroxyl groups. From the curve of mellite and alum it appears that Portland cement is too transparent beyond 3 μ to contain 17 molecules of water of crystallization, as indicated in the aforesaid formulæ.

MANNITE ($C_6H_8(OH)_6$).

(t = 0.05. Curve *a*, fig. 31.)

This substance is a hexahydric alcohol. The film examined was a semi-transparent (due to crystallization) solid, between rock-salt plates. The transmission curve has the general characteristics of the alcohols,

[1] Le Chatlier: Annales des Mines, Feb., 1888.

which have a wide band from 3 to 4 μ and a transparent region from 4.5 to 5.5 μ, followed by opacity beyond 6 μ.

It is known that for alcohols the large band in the region of 3 μ is the composite of two bands situated at 3 and at 3.43 μ.

CHLORAL HYDRATE ($CCl_3CH(OH)_2$). (Curve *b*, fig. 31.)

The constitution of this compound is uncertain. For the present examination the crystals were melted between plates of rock salt, and placed over P_2O_5 to dry and recrystallize. The transmission curve shows all the water bands; although it is not considered water of crystallization, curve *c* shows the region at 3 μ after the film stood over P_2O_5 for six days and had crystallized into an opaque mass. Chloral

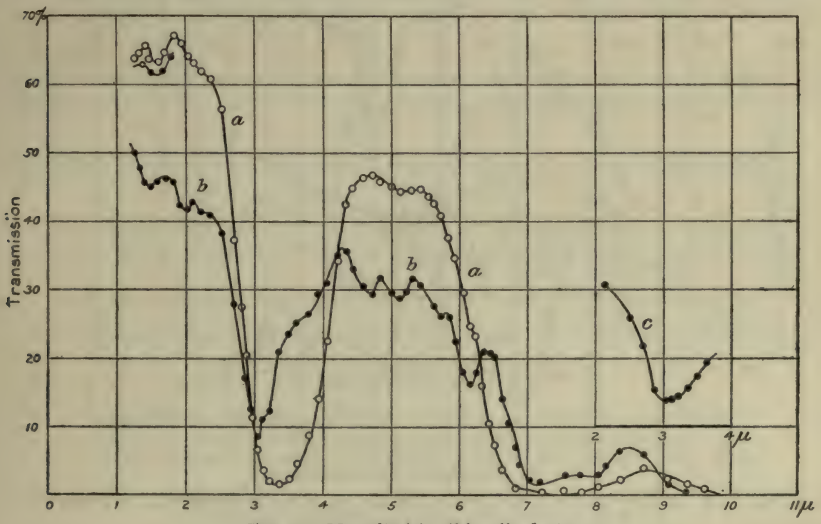

FIG. 31.—Mannite (*a*); Chloralhydrate.

hydrate has the following bands: 1.5, 2, 3, 3.2, 3.7, 4.7, 5.1, 5.7, 6.2, 7.2, and 8 μ. Curve *c* is *b* after crystallizing several days.

In the foregoing dozen minerals containing hydroxyl groups there is only one, or possibly two, viz, manganite and datolite, which appear to be exceptions to the rule that hydroxyls have a band at 3 μ. It will, of course, be understood that this decision is also based upon previously studied compounds referred to in the text.

Several other minerals in which the constitution is less understood, but which are supposed to contain hydroxyl groups, for example serpentine and epidote, will be considered later on, where it will be found that the 3 μ band is also very evident.

PREHNITE ($H_2Ca_2Al_2(SiO_4)_3$).

(Stalactitic; light green, translucent, crystalline mass; $t = 0.78$ mm. Curve *a*, fig. 32.)

We have now to consider a series of hydrous silicates in which the oxygen and hydrogen are supposed to exist as such in the molecule. It will be noticed that the SiO_2 radical does not give sharp bands that are in a fixed position—e. g., at 2.9 μ.

Prehnite has bands at 2.9, 4.15, 5.96, and 7.3 μ, but none coincide with the water bands. It so happens that in this mineral the bands coincide very closely with those found in quartz.

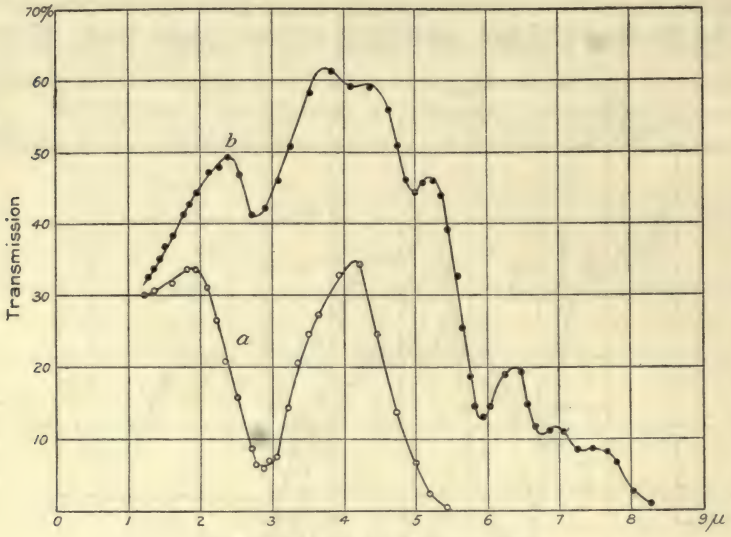

FIG. 32.—Prehnite (*a*); Hydronephelite.

HYDRONEPHELITE ($HNa_2Al_2(SiO_4)_3+3H_2O$).

(From Litchfield, Massachusetts. Massive dark-gray material; subtranslucent in section of 0.12 mm. Curve *a*, fig. 32.)

This substance is supposed to contain water of crystallization, but the general outline of the transmission curve does not show it. Possibly it is an hydroxide. The general appearance of the material did not appear to warrant a further inquiry into this apparent exception to the rule. There is a wide band at 2.9 μ. Water is expelled at a high temperature.

PECTOLITE ($HNaCa_2(SiO_3)_3$).

(Translucent sections; $t = 1.0$ and 0.25 mm. Curves *a* and *c*, fig. 33. From Bergen Hill, New Jersey.)

Curve *a* is for a monoclinic prismatic cleavage piece, while curve *c* is for a mass of needles all of which came from the same piece. The two

do not give coincident results, but there being no bands near those of water, it did not seem worth while to make further inquiry.

CHLORITOID ($H_2(MgFe)Al_2SiO_7$).

(Variety, masonite; cleavage piece parallel to *c*; transmits blue-green; $t = 0.25$. Curve *b*, fig. 33.)

This mineral is very opaque to infra-red radiation. There are several small absorption bands, viz, at 2.3, 2.6, 3.3, 5, 6, and 6.3 μ, as in the preceding. The point of interest is the absence of bands at 1.5 and 3 μ.

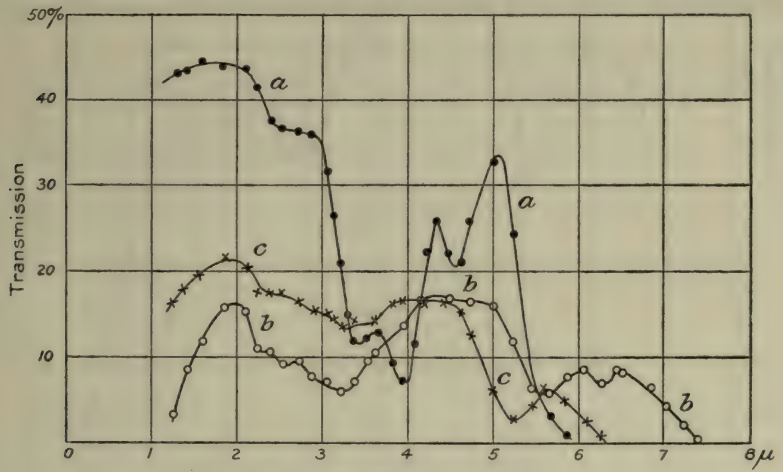

FIG. 33.—Pectolite (*a*); Chloritoid

CLINOCHLORE ($H_8Mg_5Al_2Si_3O_{18}$); PENINITE ($H_8MgFe)_5Al_2Si_3O_{18}$).

(Clinochlore: $t = 0.08$. Peninite: curve *b*, $t = 0$ mm. Fig. 34.)

These two minerals belong to the chlorite group, which is related to the micas, to be noticed presently. These minerals contain about 12 per cent of water, which is given off at a high temperature. Their transmission curves are unusually similar to those of the micas. There are absorption bands at 2.9, 5.9, 6.3, 7.1, and 7.8 μ. The frequently recurring bands at 2.9 and 5.9 μ, with the metallic reflection band at 8.5 and 9.02 μ, remind one of harmonic series.

It may be that these bands belong to a slowly conveying spectral series, if not a harmonic series, for the first band oscillates between the values 2.8 and 2.95 μ, while the next band shifts from 5.6 to 5.9 μ, as will be noticed in the micas.

As already mentioned, the constitution of many minerals is still doubtful. Clinochlore is one of these. From investigations made by Clarke and Schneider, it was inferred that the hydroxyl groups MgOH and

$Al(OH)_2$ are present.[1] In the present examination there is no indication of a band at 3 μ, which is a characteristic of the OH radical.

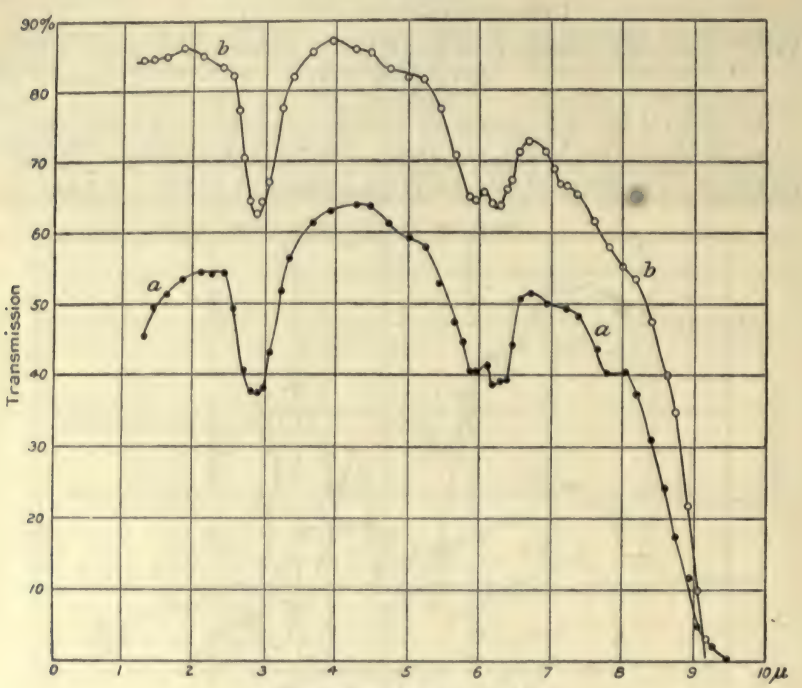

FIG. 34.—Clinochlore (*a*); Peninite.

TOURMALINE ($H_6Na_2Fe_4B_6Al_8Si_{12}O_{62}$).

(Cut parallel to optic axis. Fig. 35.)

These curves are due to Merritt (loc. cit.), and show the variation in transmission for the ordinary ray (plotted o–o–o), for the extraordinary (x–x–x), and for unpolarized light. The important absorption bands are at 1.28 and 2.82 μ. The latter is to be noticed in considering the effect of SiO_2, SiO_3, and SiO_4 groups.

MICA; MUSCOVITE, $H_2KAl_3(SiO_4)_3$; BIOTITE, $(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$.

(Cleavage parallel to *c*; curve *a*, muscovite; $t = 0.02$ and 0.04 mm; curve *b*, biotite, $t = 0.03$ mm. Fig. 35.)

The constitution of the micas is involved in a greater or less degree of uncertainty. They are all silicates of aluminium, and either K, Na, Li, or of Fe and Mg. All the micas yield water upon ignition, but it is uncertain whether this water of constitution is due to the presence of

[1] Clarke and Schneider: American Journ. Sci., 40, 405, 1890.

H or OH. There is no deep, wide absorption band at 3 μ, so that, judging by the present method of examination, there can not be any hydroxyl groups present.

Muscovite has a deep, narrow band at 2.85 μ, and smaller bands at 1.9, 3.6, 5.6, 5.9, 6.3, and 7.1 μ. Biotite has small bands at 2.8, 5.9, 6.2, and 6.7 μ, and indications of bands at 5.6 and 7 to 8 μ. It has also a band in the visible spectrum.

Both micas have a large opaque region at 9 to 11, followed by a transparent region at 12 μ, beyond which there is again complete opacity. Rubens and Nichols[1] have found metallic reflection bands at 8.32,

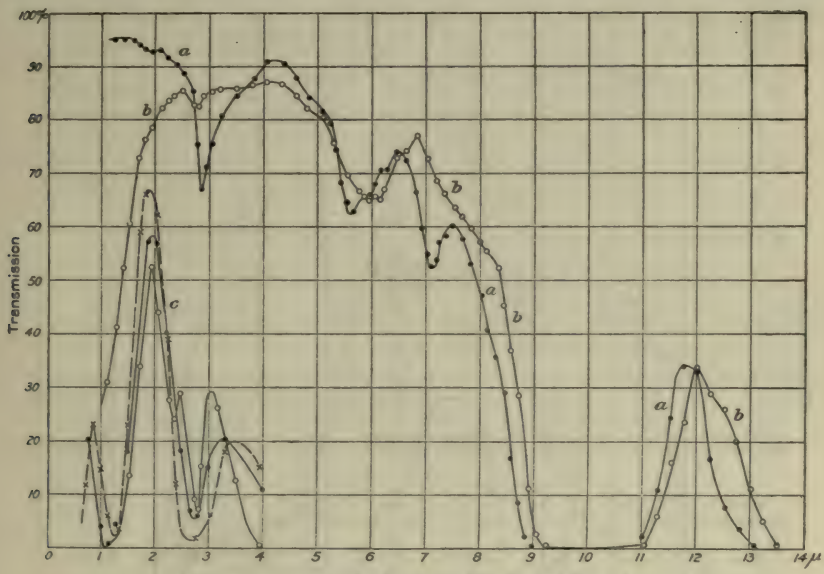

FIG. 35.—Muscovite (*a*); Biotite (*b*); Tourmaline (*c*).

9.38, 18.40, and 21.25 μ. It will thus be noticed that the bands located by reflection and by transmission do not coincide, as is to be expected, since we are in regions of anomalous dispersion.

The spectrum energy curves, found by the writer[2] using a rock-salt prism, and a radiometer having windows of the same material, never showed a sharp depression at 2.8 μ, while those found by Stewart,[3] using a fluorite prism and a radiometer having an inner window of muscovite mica and an outer one of fluorite, contained a conspicuous depression in this region. The discrepancy was explained on the

[1] Rubens and Nichols: Ann. der Phys. (3), 60, p. 418, 1897.
[2] Nichols and Coblentz: Phys. Rev., 17, p. 267, 1903.
[3] Stewart: Phys. Rev. 13, p. 261, 1901.

assumption of a larger dispersion, and a longer column of air traversed by the rays, which would intensify the CO_2 band at 2.75 μ.

From the muscovite curve, however, it will be noticed that the air (CO_2) band would be intensified by that of mica at 2.85 μ.

SERPENTINE ($H_4(Mg,Fe)_6SiO_9$).

(Massive; subtranslucent; curve *a*, $t = 0.225$ mm; curve *b*, $t = 0.08$ mm. Fig. 36. From Montville, New Jersey.)

In serpentine the water is chiefly expelled at red heat. According to Miers,[1] talc and serpentine are to be regarded as basic and not hydrated

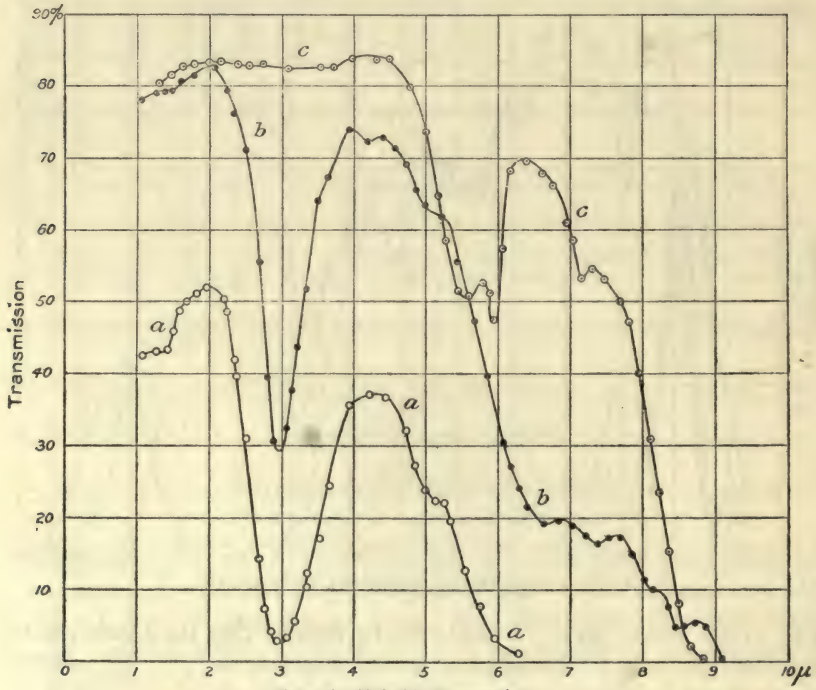

FIG. 36.—Talc (*c*); Serpentine.

silicates, since they part with their water only at a high temperature. From the curve of serpentine, which shows a large absorption band at 3 μ, if the results from the present method of examination are to be trusted, it would appear that there are hydroxyl groups present.

From the results obtained by Clarke and Schneider[2] it was inferred that the Mg is present as MgOH, and hence the formula is written $H_3(MgOH)$, $Mg_2(SiO)_2$. It has also been written with two mag-

[1] Miers: Mineralogy, p. 439.

[2] Clarke and Schneider: Amer. Jour. Sci., 40, p. 308, 1890.

nesium hydroxyl groups. Serpentine has absorption bands at 1.4, 3, 5, 6.6, 7.4, 8.1, and 8.5 μ.

TALC ($H_2Mg_3SiO_{12}$).

(Subtransparent; $t = 0.06$ mm. Curve *c*, fig. 36.)

In talc, water is expelled at red heat; from its stability with acids it is considered an acid metasilicate. From the investigations of Clarke and Schneider (loc. cit.) no hydroxyl groups were inferred, and the trans-

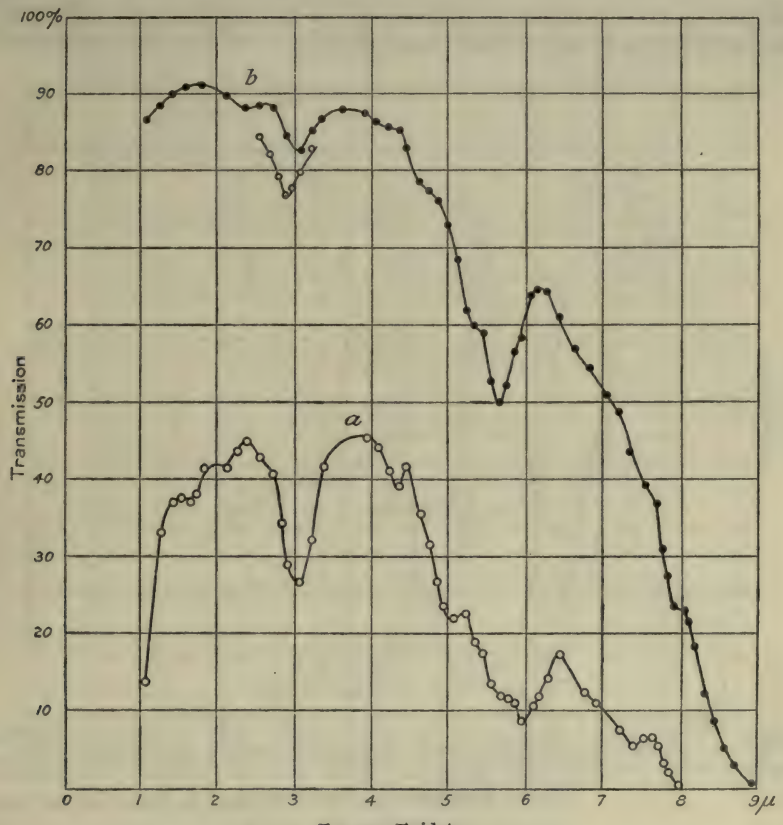

FIG. 37.—Epidote.

mission curve does not show a band at 3 μ. Talc has absorption bands at 5.6, 5.95, and 7.15 μ.

EPIDOTE ($Ca_2(AlOH)(Al,Fe)_2(SiO)_3$).

(Cleavage piece parallel to *c* for curve *a*, $t = 0.21$; section perpendicular to axis for curve *b*, $t = 0.09$. Fig. 37.)

The chemical formula of this mineral is variously written, and it may contain hydroxyl groups. The iron may be present as FeOH.

In the present examination curve *a* is for a section transmitting a brown color, while curve *b* was light green. Both show the hydroxyl band at 3 μ, while additional bands occur at 4.3, 4.7, 5.0, 5.3, 5.6, 5.9, 6.6, and 7.4 μ, many of which are in common with those of quartz.

SODIUM METAPHOSPHATE ($NaPO_3$).

(Fused transparent glass; $t = 0.37$. Fig. 38.)

This substance was examined in connection with the following phosphates to learn the behavior of phosphorus in a compound. There is a wide absorption band at 4 and a second at 6 μ.

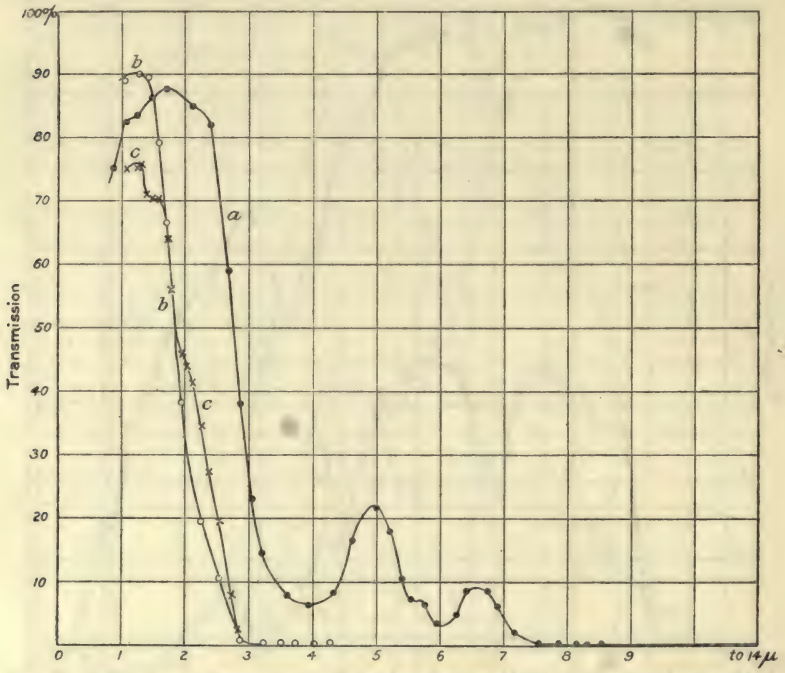

FIG. 38.—Sodium metaphosphate (*a*); Meta phosphoric acid (*b*); Ortho phosphoric acid (*c*).

META PHOSPHORIC ACID (HPO_3).

($t = 0.25$ mm. Curve *b*, fig. 38.)

This substance comes in transparent cylindrical sticks like KOH. It was melted between a plate of rock salt and one of glass. The latter became loose on cooling, and was removed. The compound is too opaque for examination beyond 3 μ.

ORTHO PHOSPHORIC ACID (H_3PO_4).

($t = 0.12$ mm. Curve *c*, fig. 38.)

This compound is formed from HPO_3, and also from P_2O_5, standing in moist air.

In both cases the curves *b* showed the water bands at 1.5 and 2 μ, beyond which there was complete opacity.

Group III: Miscellaneous Compounds.

It has been noticed elsewhere that in the examination of selenite the large absorption band at 4.55 μ is shifted, and too deep to belong to water; also that it was suspected to be due to the SO_4 groups of atoms. The band has further been noticed in discussing selenite and anhydrite (fig. 3), and in thaumasite and blödite (fig. 13). Under the present heading will be discussed the absorption spectra of simple sul-

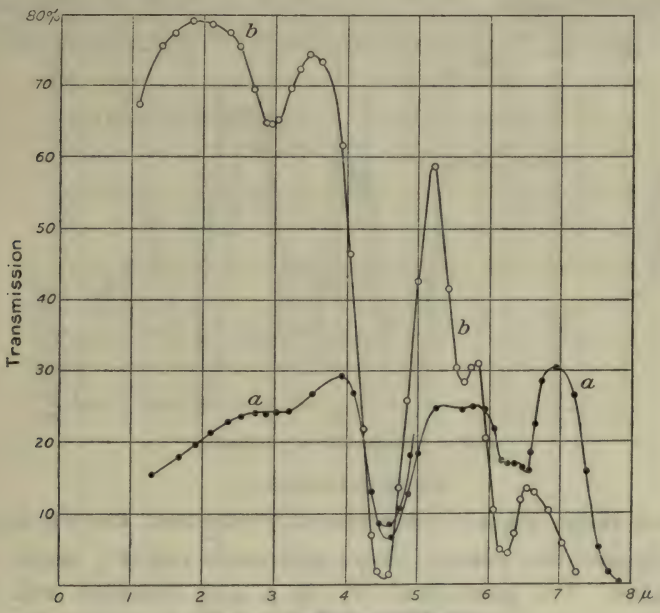

Fig. 39.—Barite (*a*); Glauberite.

phates formed by the combination of a metallic oxide and sulphur trioxide, all of which show a band at 4.55 μ, while several have another band in common at 6.5 μ.

SULPHATES.

Barite ($BaSO_4$).

(Orthorhombic; section parallel to *c*; translucent; $t = 0.25$. Curve *a*, fig. 39. From Cheshire, Connecticut.)

The barite curve is quite opaque, due in part to numerous cracks. There are bands at 3, 4.6, 6.2, and 6.5 μ. Königsberger's curves show that the band at 4.6 μ is wide, and shifts for different directions of vibration of polarized light.

GLAUBERITE ($Na_2SO_4CaSO_4$).

(Monoclinic; cleavage section parallel to *c*; transparent; $t = 1.26$. Curve *b*, fig. 39).

This is a mixture of two sulphates, of which the $CaSO_4$ band at 3.2 and 4.55 μ have already been noticed. Glauberite has bands at 3, 4.55, 5.6, and 6.2 μ.

THENARDITE (Na_2SO_4).

(Borax Lake, California. Orthorhombic; ground parallel to *c*; $t = 2.2$ mm. Curve *a*, fig. 40.)

This mineral was too brittle to grind successfully. It shows large bands at 3.1 and 4.55 μ.

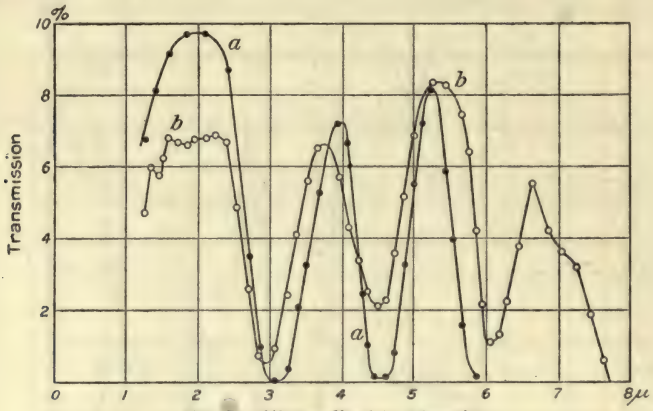

FIG. 40.—Thenardite (*a*); Kieserite.

KIESERITE ($MgSO_4$).

(Stassfurt Mines. Massive; subtranslucent; $t = 0.22$ mm. Curve *b*, fig. 40.)

This mineral, like selenite, shows both water and SO_4 bands. It is very opaque. The water bands at 1.5, 3, 4.55 (complex with SO_4), and 6.05 μ are prominent. There are two small bands at 1.8 and 7 μ, respectively.

CELESTITE ($SrSO_4$).

(From Lampasas, Texas. Cleavage parallel to *c*; transparent; $t = 0.67$ mm. Curve *a*, fig. 41.)

Celestite has absorption bands at 3.2, 4.55, and 6.4 μ. The 4.55 μ band is conspicuous for its depth.

ANGLESITE ($PbSO_4$).

(Monte Poni, Sardinia. Translucent; section parallel to *m*; $t = 0.7$ mm. Curve *b*, fig. 41.)

The section used was not quite long enough to cover the slit. The lack of transparency was in part due to the fact that on account of its

brittleness the section was not highly polished. The band at 4.55 μ is complex, with a deeper one at 5 μ. The same is true of the 6.4 μ band, which is complex, with a stronger band at 6.7 μ. There are slight depressions at 1.9 and 3.2 μ.

Cadmium Sulphate ($3CdSO_4+8H_2O$).

(Curves *a*, *b*, *c*, *d*, fig. 42; $t=0.98$ and 0.1 mm.)

This was an artificially grown crystal, and was perfectly transparent. As a whole, it is very opaque to infra-red radiation. The band at 3 μ is complex, as is also the one at 4.6 μ, which is shown in curve *d*, the vertical scale of which is magnified 10 times. The water bands at 1.5 and 2 μ are well defined, considering the opacity of the substance.

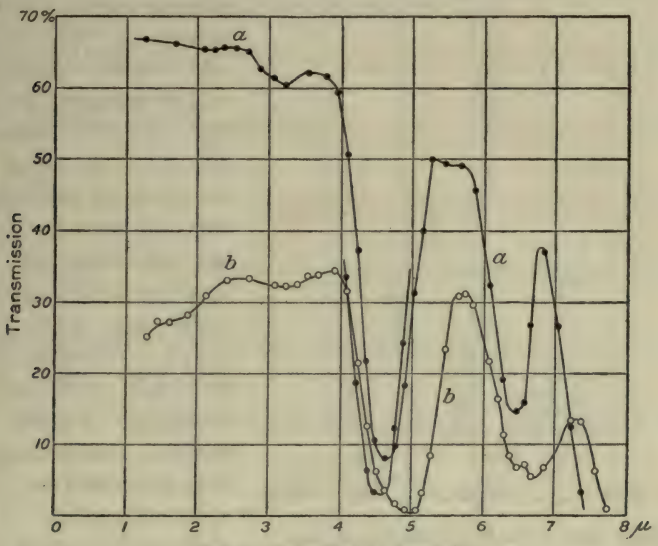

Fig. 41.—Celestite (*a*); Anglesite.

Sulphuric Acid (H_2SO_4).

(Curve *e*, fig. 42.)

The great opacity of this substance makes it difficult for examination. A film, 0.08 mm. in thickness, was pressed between two plates of cover-glass, and stood over P_2O_5 for several days. It shows no water bands, while the trend of the curve at 4.5 μ makes it impossible to decide on the question of the SO_4 band. There is a band at 3.6 μ which is broad and shallow.

It is difficult to decide whether the frequently recurring bands at 6.2 and 6.5 μ are due to SO_4; but it is a fact that they are very conspicuous

in the sulphates examined, especially for K, Ba, Ca, and Pb, which have a common band at 6.5 μ.

The sulphates of the metals K, Rb, and Cs have been compared by Tutton,[1] who has shown that both as regards crystalline form, specific gravity, thermal expansion, and corresponding refractive indices the Rb salt lies between the K and Cs salts. These monovalent elements occupy consecutive positions in the even series of Mendeleef's table. The next even series is Ca, Sr, and Ba, the transmission curves of which are before us. The following odd series contains Mg, which just precedes Ca and Cd, which lie between Sr and Ba. In other words, the elements lie in the order Mg, Ca, Sr, Cd, Ba, while the maximum of the absorption band occurs in the order 4.5, 4.55, 4.6, 4.6, 4.63 μ. Whether this is a true shift, with increase in molecular weights, needs further examination. The data presented are certainly very suggestive of a real shift, with increase in molecular weight of the metal. This same shifting of the maximum, with increase in molecular, will be noticed in the *reflection* curves of $SrSO_4$ and $BaSO_4$; in the former the maxima are at 8.2, 8.75, and 9.05 μ, while in the latter the maxima are shifted to 8.34, 8.9, and 9.1 μ.

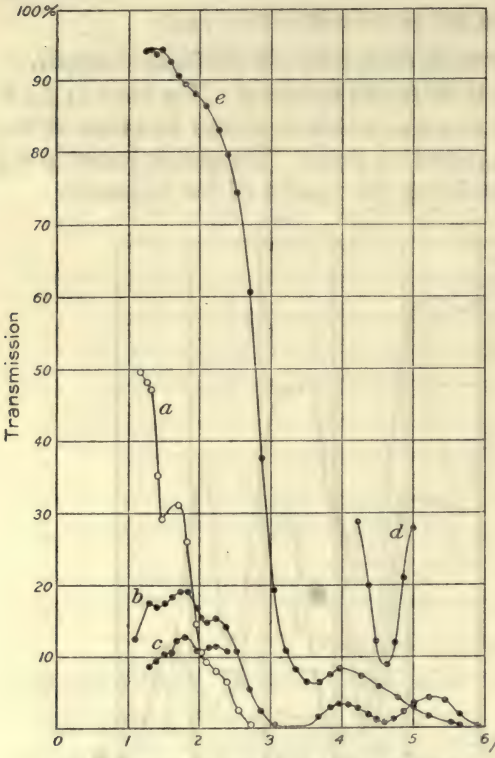

FIG. 42.—Sulphuric acid (*e*); Cadmium sulphate.

Drude[2] has shown that in the ultra-violet the absorption band is due to the sympathetic vibrations of particles which have a charge and mass identical with the "ion" (or "corpuscle"), while, in the infra-red, the absorption bands are due to particles which have a mass of the order of magnitude of the molecule. From this standpoint one would expect

[1] See Miers, Mineralogy.

[2] Drude: Ann. der Phys. (4), 14, p. 677, 1904.

to find a shift of the maximum toward the longer wave-lengths, as we increase the atomic weight of the element which is attached to the radical.

MISCELLANEOUS COMPOUNDS.

Potassium Dichromate (K_2CrO_7).

(Cleavage parallel to m; $t = 0.85$ mm. Fig. 43.)

It was found that this substance furnished beautiful, highly polished cleavage pieces, which are quite transparent to infra-red radiation. The curve shows a complex depression at 2.9 to 3.2 μ, and bands at 5.4, 6, 6.65, 7.7, and 8.7 μ.

Porter[1] located a reflection band at 10.3 μ.

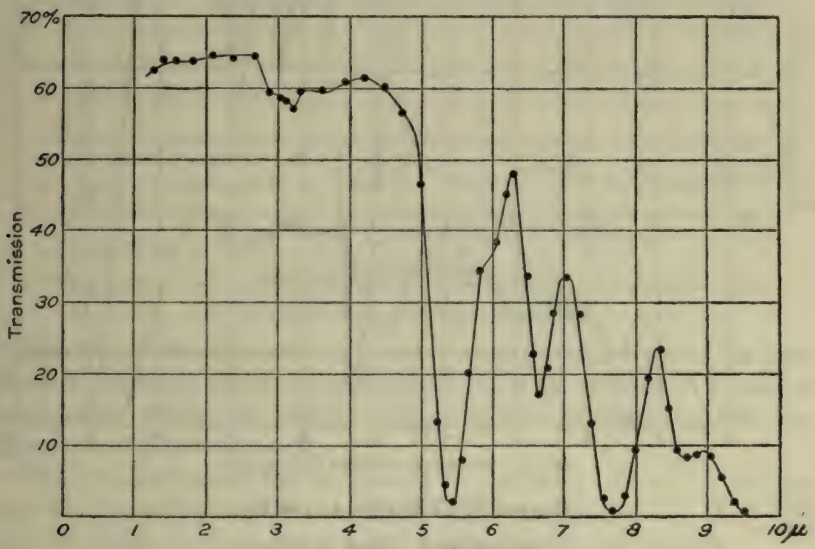

Fig. 43.—Potassium dichromate.

Potassium Chlorate ($KClO_3$).

(Large transparent crystal; $t = 0.47$ mm. Curve a, fig. 44.)

The absorption bands in this substance are strikingly similar to those of potassium dichromate, especially the 5.25 μ band, which is shifted to 5.4 μ in the latter. There are bands at 3.2, 3.5, 5.25, 6.28, 6.93, and 8.1 μ, beyond which there is complete opacity.

[1] Porter: Astrophys. Jour., 22, p. 229, 1905.

APATITE ($Ca_5F(PO_4)_3$).

(From Kragerve, Norway. Massive; subtranslucent; $t = 0.12$ mm. Curve *b*, fig. 44.)

There are no strong bands in this mineral, and none are found to be common with substances containing the PO_4 radical. The bands are small and occur at 2.9, 3.9, 4.85, 5.85, 6.4, and 6.85 μ.

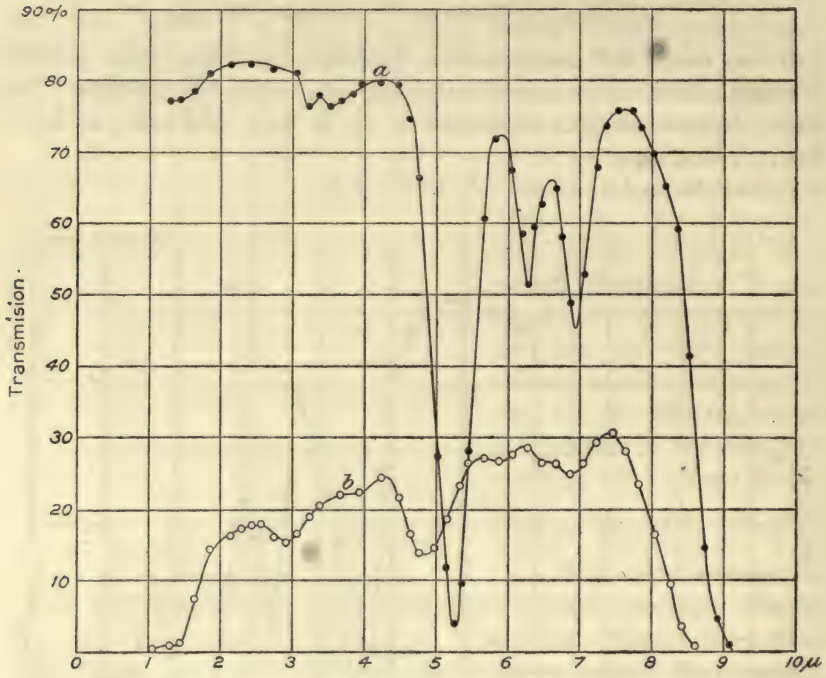

FIG. 44.—Potassium chlorate (*a*); Apatite.

GARNET ($Ca_3(Fe,Mg)_3Al_2(SiO_4)_3$).

($t = 3.25$ mm. Curve *a*, fig. 45.)

This garnet was wine-red in color, showing absorption bands in the yellow-green and in the green-blue parts of the spectrum.

The transmission curve is extraordinary, having a wide absorption band extending from 1.2 to 2.6 μ, and complete opacity beyond 4.5 μ.

MONAZITE, $(Ce,La,Di)PO_4$.

($t = 1.04$ mm. Curve *b*, fig. 45.)

This brown-colored mineral was partly transparent to visible rays, and is equally opaque to infra-red rays. A large band extends from 3.5 to 5.5 μ, and opacity beyond 6.5 μ.

WILLEMITE (Zn_2SiO_4).

(From Parker Shaft, Franklin, New Jersey. Semi-transparent; $t = 0.08$ mm. Curve *c*, fig. 45.)

The sample was a mixture of calcite and willemite. The section examined was quite pure willemite. The curve shows a depression at 2.9 μ and bands at 5.9 and 6.75 μ.

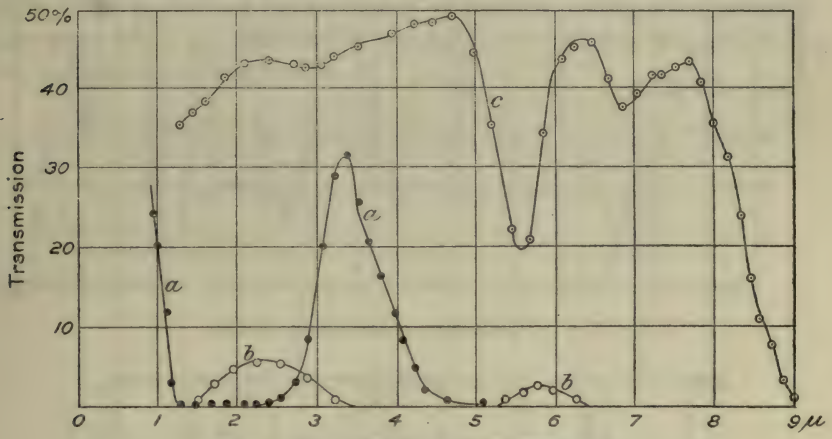

FIG. 45.—Garnet (*a*); Monazite (*b*); Willemite.

COLLODIUM ($C_6H_7O_2(ONO_2)_3$).

($t = 0.01$ mm. Curve *a*, fig. 46.)

The film of this compound was made by painting a layer of the commercial "collodion" over a rectangular hole, 4 by 10 mm., in a piece of cardboard. After the volatile solvent had evaporated the film was dried over P_2O_5 for a week.

The constitution of this compound is unknown. It will be noticed that the transmission curve is entirely different from those rich in CH_2 or CH_3 groups or from those found for the benzine derivatives.

There are absorption bands at 1.65, 2.9, 3.5, 6.05, 7.3, 7.85, 8.7, 9.2, 9.5, 10.0, 10.8, 11.7, 12.3, 12.7, and 13.6 μ.

AMMONIUM CHLORIDE (NH_4Cl).

(Translucent; $t = 0.6$ mm. Curve *b*, fig. 46.)

Section made from a lump of the commercial material. It is very opaque, with bands at 1.65, 2.2, and 2.95 μ, the latter being in the region where NH_2 compounds and NH_3 have a band. Porter (loc. cit.) found a reflection band at 3.44 μ.

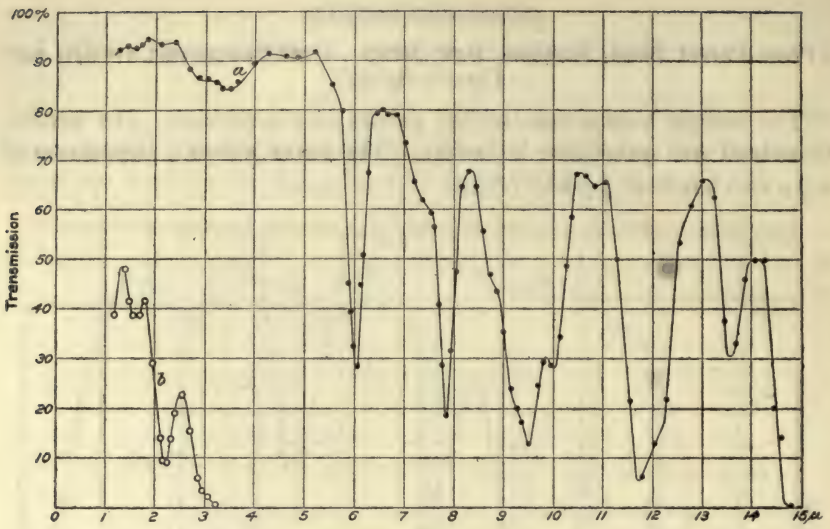

FIG. 46.—Collodium (*a*); Ammonium chloride.

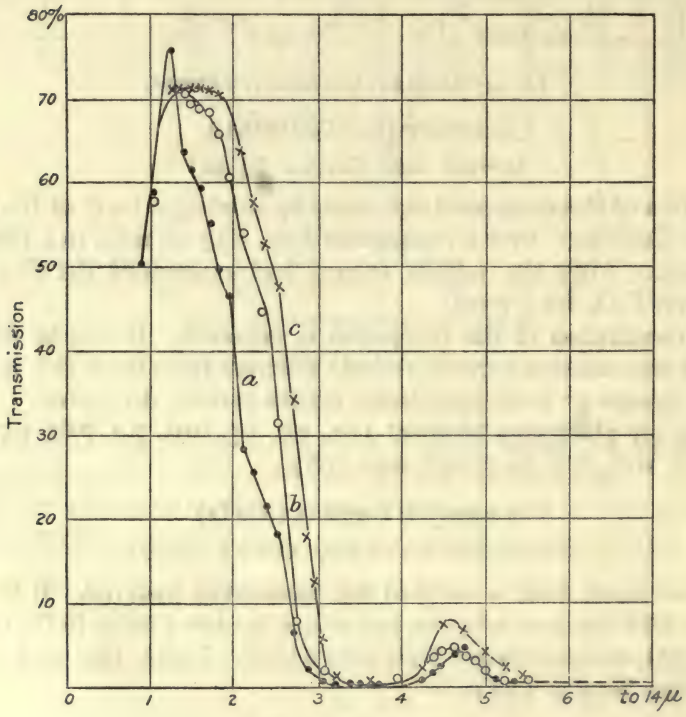

FIG. 47.—Tartaric acid.

TARTARIC ACID ($C_4H_6O_6$).

(Cleavage parallel to *a*. Curve *a*, fig. 47.)

In fig. 47 curve *c* is for a film melted and crystallized between thin cover-glass, $t = 0.09$ mm., while curve *a* is for a cleavage section, $t = 0.32$ mm. Curve *b* is for a film melted between plates of rock salt. This compound has the properties of a divalent alcohol and of dibasic acids. The curves are characteristic of alcohols, having an absorption band from 2.9 to 4 μ, followed by a transparent region at 4.6 μ, which is characteristic of carbohydrates.

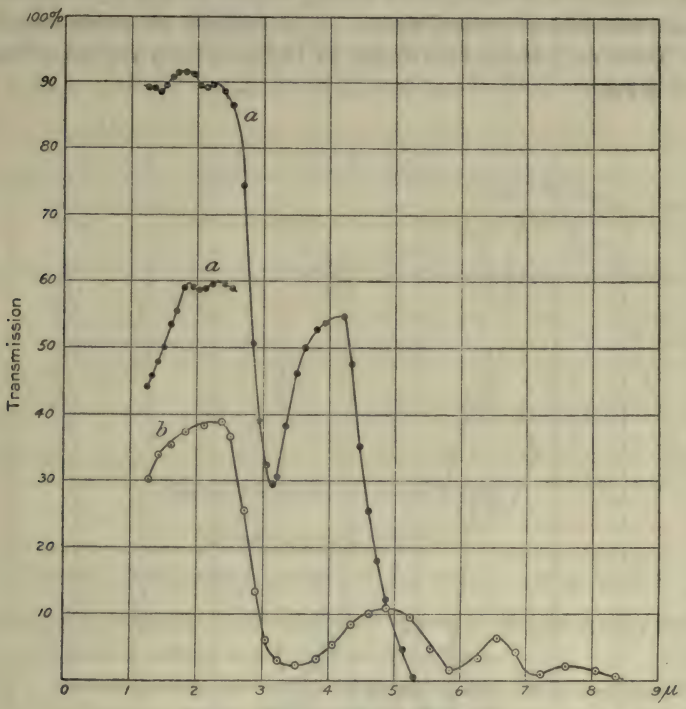

FIG. 48.—Phloroglucin (*a*); Malic acid.

PHLOROGLUCIN ($C_6H_3(OH)_3+2H_2O$).

($t = 0.02$. Fig. 48.)

This belongs to the group containing water of crystallization. Apparently it is an exception to the rule. The sample turned light brown on melting, and it is quite probable that the H_2O was partly expelled. The compound belongs to the phenols, hence one would expect a band at 3 to 3.2 μ, the latter being the characteristic of benzine. There are small water bands at 1.45 and 2.05 μ.

MALIC ACID ($C_2H_3(OH)(CO_2H)_2$).

($t = 0.08$. Curve *b*, fig. 48.)

This compound belongs to the trivalent dibasic acids ($C_nH_{2n-2}O_5$), and, like the acids previously studied, is very opaque, with wide absorption bands at 3.5, 5.9, and 7.2 μ.

SODIUM BIBORATE ($Na_2B_4O_7$).

(Fused glass, transparent, ground to $t = 0.12$ mm. Curve *a*, fig. 49.)

This compound is formed on fusing borax ($Na_2B_4O_7$), which contains 10 molecules of crystal-water. It is difficult to decide whether or not the bands at 3 and 4.8 μ are due to H_2O. There are other bands at 1.9 and 3.7 μ.

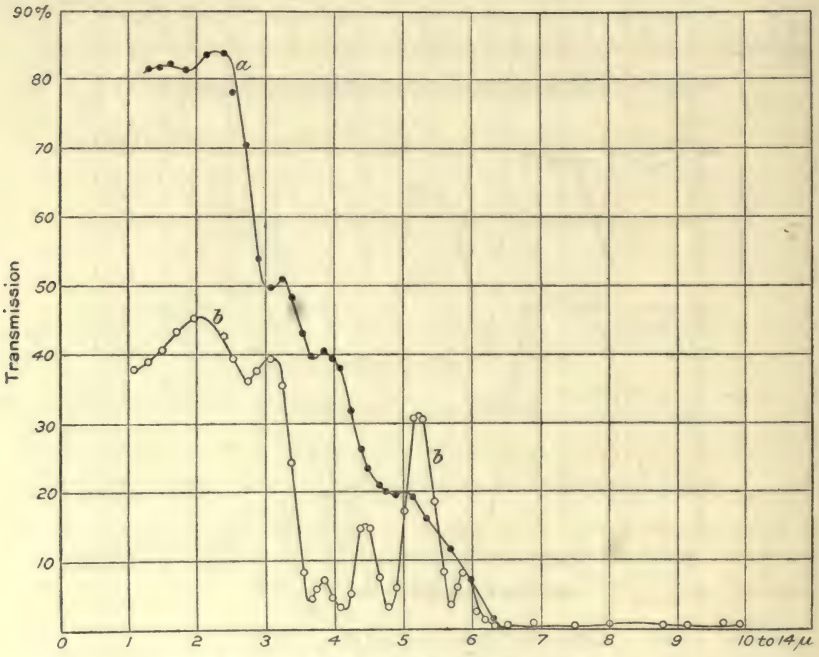

FIG. 49.—Sodium biborate (*a*); Silver nitrate.

SILVER NITRATE ($AgNO_3$).

($t = 1.65$ mm. Curve *b*, fig. 49.)

This crystal was ground, but not highly polished. Its transmission curve is marked for its sharp bands at 2.7, 3.6, 4.1, 4.78, and 5.65 μ.

SPHALERITE (ZnS).

(Cleavage piece, $t = 1.53$ mm.; transparent; slightly yellowish tinge. Curve *a*, fig. 50.)

The transmission curve is marked for its extraordinary transparency from 5 to 12 μ, interrupted by slight depressions at 1.6, 11.2, and 13.2 μ. There is a wide band from 2.7 to 3.3 μ, and complete opacity beyond 15 μ.

SILVER CHLORIDE (AgCl).

(Vitreous, $t = 0.8$ mm. Curve *b*, fig. 50.)

This is the only known substance for which no absorption bands have yet been found in the infra-red. It seems to increase in transparency with increase in wave-length, but is opaque for the "reststrahlen" at 53 and 61 μ, as one would expect from its analogy to NaCl and KCl.

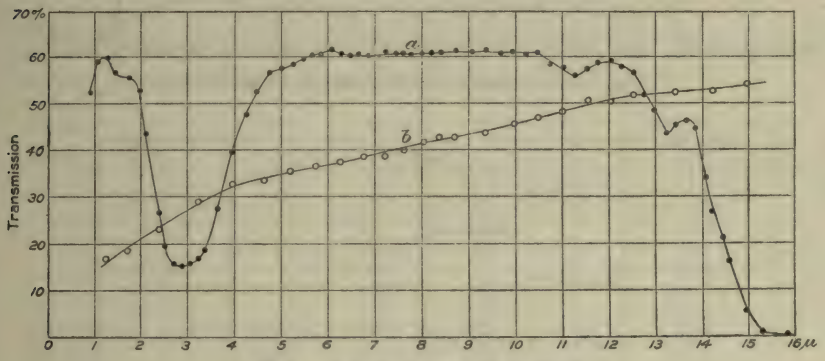

FIG. 50.—Sphalerite (*a*); Silver chloride.

ORTHOCLASE ($KAlSi_3O_8$).

(Yellowish tinge; subtransparent; $t = 0.07$ mm. Curve *a*, fig. 51.)

This mineral belongs to the feldspar group. It has bands at 2.85, 4.7, 5.7, and 6.28 μ, which are bands of silicates.

Curve *c*, $t = 0.23$ mm., is for a cleavage piece from a specimen of unknown composition, and was simply marked "Feldspar." It has the general outline of, but the bands are less marked than in, curve *a*.

AMPHIBOLE ($CaMg_3(SiO_3)_4$).

(Silky gray color, probably tremolite; ground parallel to *m*; translucent; $t = 0.07$ mm. Curve *b*, fig. 51.)

This curve is similar to orthoclase, with bands at 2.8, 4.8, 6, 7.4, and 8.2 μ. The 6 μ band may be the mean of the two found in orthoclase, at 5.7 and 6.28 μ, respectively.

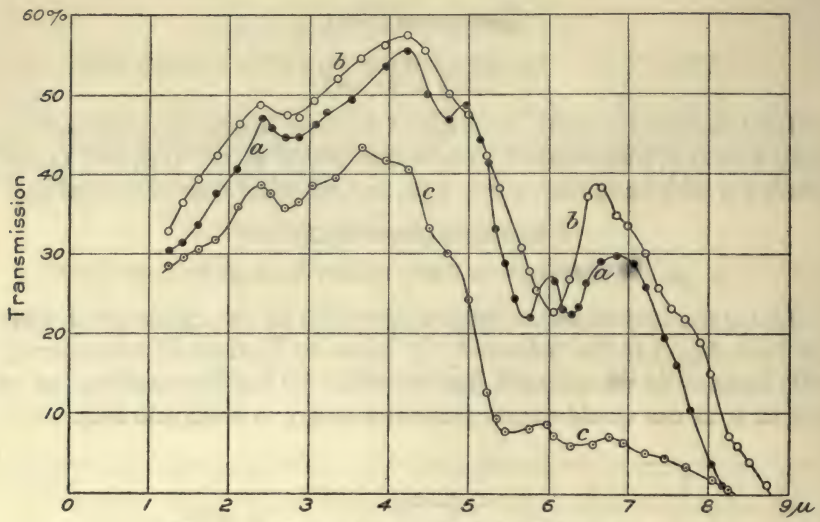

FIG. 51.—Orthoclase (*a*); Amphibole (*b*); Feldspar (*c*).

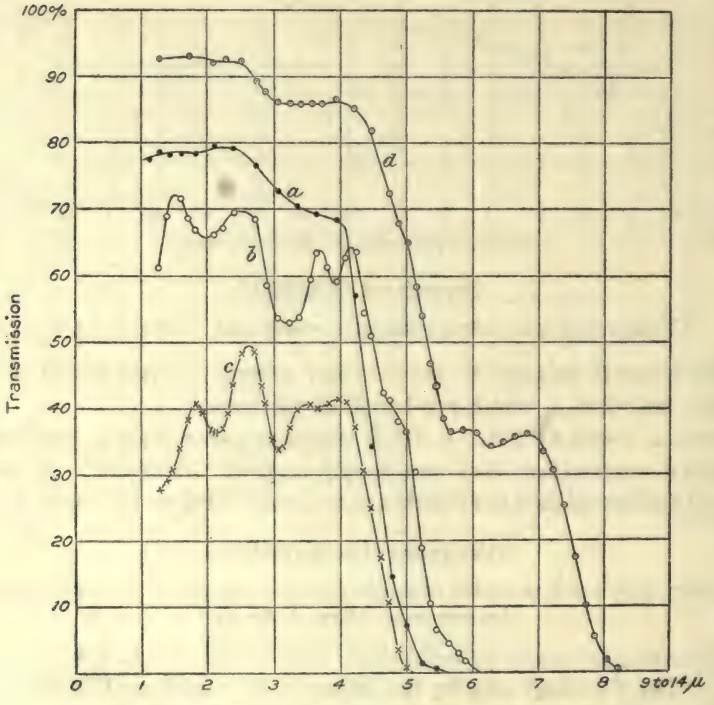

FIG. 52.—Oligoclase (*a*); Orthoclase (*b*); Zircon (*c*); Glass (*d*).

OLIGOCLASE $\left\{\begin{matrix}3NaAlSi_3O_8.\\CaAl_2Si_2O_8.\end{matrix}\right.$

(From Bakersville, North Carolina. Cleavage piece; not polished; transparent; $t = 1.25$ mm. Curve *a*, fig. 52.)

This mineral has no marked absorption bands. There is a depression in the transmission curve at 3.3 μ.

ORTHOCLASE (var. ADULARIA) ($KAlSi_3O_8$).

(From St. Gothard, Switzerland. Cleavage parallel to *c;* perfectly transparent; $t = 0.15$ mm. Curve *b*, fig. 52.)

The transmission curve shows bands at 2.0, 3.2, 3.9, 4.8, and 5.6 μ, and is in marked contrast with the orthoclase curve.

ZIRCON ($ZrSiO_4$).

(Transparent; $t = 3$ mm. Curve *c*, fig. 52.)

This specimen was not long enough to cover the slit. It shows bands at 2.1, 3.1, and 3.6 μ, and complete opacity beyond 5 μ.

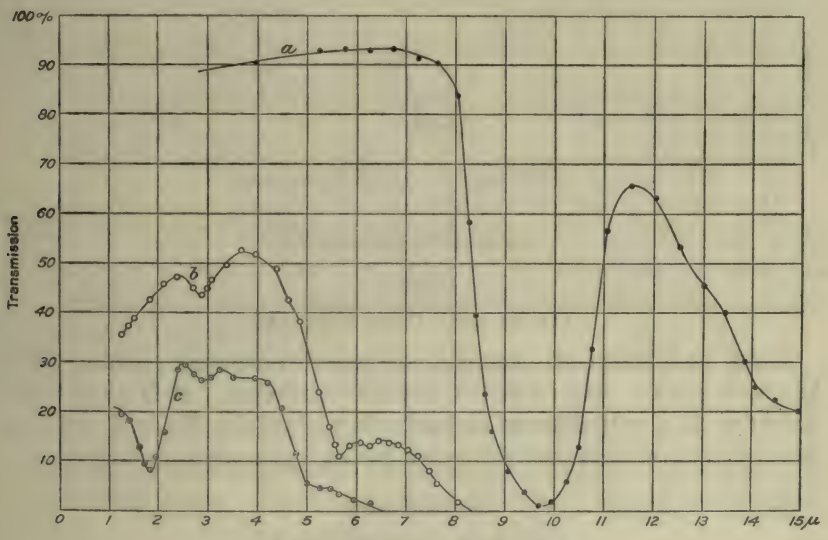

FIG. 53.—Glass (*a*); Albite (*b*); Enstatite (*c*).

GLASS.

(Microscope cover-glass; $t = 0.09$ mm. Curve *d*, fig. 52; curve *a*, fig. 53. $t = 0.001$ mm.)

The transparency of glass is very great up to 2 μ. The curve shows a depression at 3.2 μ, and bands at 5.6 and 6.25 μ, which are common to SiO_2 compounds. For this thickness glass is transparent to 8 μ.

In fig. 53, curve *a*, is shown the transmission curve or ordinary soft glass which has been blown into a bulb of such a thickness that it showed interference colors. This is the thinnest film yet examined. There is one large complex absorption (reflection) band extending from 8.5 to 10.7 μ, the maximum being at 9.7 μ.

ALBITE ($NaAlSi_3O_8$).

($t = 0.14$. Curve *b*, fig. 53.)

This mineral is more transparent than orthoclase (fig. 51, curve *a*). The absorption bands at 2.9, 5.7, and 6.3 μ coincide with those of orthoclase.

ENSTATITE ($MgSiO_3$).

("Bronzite." $t = 1$ mm. Curve *c*, fig. 53.)

This specimen was a mixture of several crystals. The transmission curve shows a large absorption band at 1.85 μ, and smaller depressions at 2.9 and 5.2 μ.

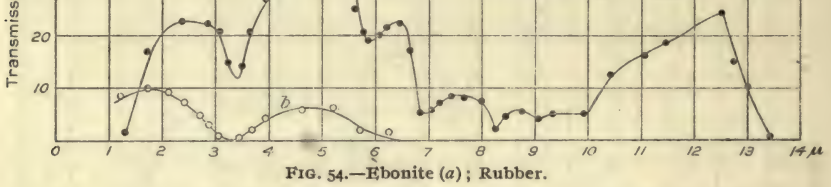

FIG. 54.—Ebonite (*a*); Rubber.

EBONITE.

($t = 0.1$ mm. Curve *a*, fig. 54.)

In fig. 54 is shown the transmission curve of ordinary ebonite, which has been ground thin, so that it was subtranslucent. It is quite transparent to 14 μ, with absorption bands at 3.4, 5.9, 6.9, 8.3, 9.1, and 10 μ, which are in coincidence with bands belonging to carbohydrates.

PARA RUBBER.

(Subtranslucent; $t = 0.27$ mm.)

In curve *b*, fig. 54, is given the transmission curve of a thin piece of sheet rubber. It is very opaque, but shows a large band at 3.3 μ.

STIBNITE (Sb_2S_3).

(Cleavage piece parallel to *b*; $t = 0.45$, 0.98 and 4.9 mm. Fig. 55.)

This is one of the most remarkable substances examined. It has a metallic luster, which is highly splendent on fresh cleavage surfaces.

It is, of course, opaque to the visible rays, but, for the thickness used, it transmits 45 to 50 per cent of the infra-red from 1.5 to 12 μ. This great transparency to heat rays seem to be a property of the sulphides, as will be noticed in sphalerite (ZnS). In this connection is to be noticed that selenium is also very transparent to heat rays.

From the reflection curve it will be noticed that the above thickness of stibnite is practically transparent, instead of transmitting only 45 per cent, as indicated above. From curves *a* and *b*, it will be noticed that there is practically no difference in the transmission, although one is twice as thick as the other. The greater transparency of the thicker film at 7 μ is not an error in observation, as was found on repeating the

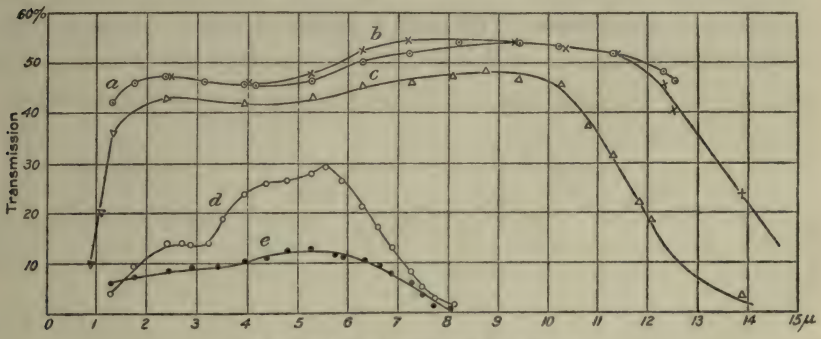

FIG. 55.—Stibnite; Brookite (*d*); Rutile (*e*).

work. In curve *c*, where the thickness is 4.9 mm., the absorption (selective reflection ?) band beyond 15 μ becomes quite evident. In this region the reflection curve suddenly decreases, indicating a region of anomalous dispersion.

BROOKITE (TiO_2).

($t = 0.37$ mm. Curve *b*, fig. 55.)

The specimen examined was subtranslucent, and by transmission was of a grayish tinge. The curve shows no bands except a depression at 3.1 μ.

RUTILE (TiO_2).

($t = 0.25$ mm. Curve *c*, fig. 55.)

The section of this mineral was ground from a long, flat needle, which transmitted a deep red. It is more opaque than brookite, from which it differs in crystalline form.

Potassium Nitrate (KNO_3).

($t = 0.32$. Curve *a*, fig. 56.)

The section of this substance was made from the commercial material. It is conspicuous for its large absorption band extending from 6.5 to 8.5 μ, and a slightly smaller band at 12 μ.

There are absorption bands at 3.6, 4.0, 4.7, 5.65, 6.5 to 8.5, 9.6, 10.2, 12.0, 13.1, and 14.3 μ. Some of these bands coincide with sharp bands in silver nitrate. The reflection curve (x–x–x–x) shows a maximum at 7.15 μ.

Amber.

($t = 0.8$ mm. Curve *b*, fig. 56.)

Amber is a fossil resin. The section examined is too opaque to give us any information.

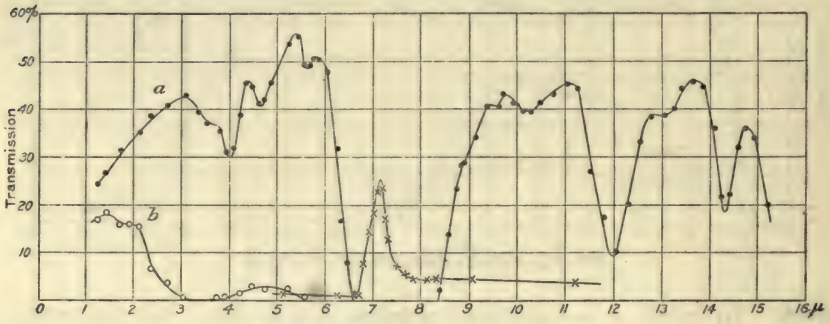

Fig. 56.—Potassium nitrate; Amber (*b*).

Fluorite (CaF_2).

In fig. 57 are shown the transmission curves of several pieces of fluorite, examined several years ago, but never published. They are given to show the difference between a perfectly white fluorite, curve *a*, and a greenish tinged variety, curve *b*. The latter shows a slight absorption band at 1.4 μ. In curve *a*, $t = 23$ mm., and in curve *b*, $t = 4.75$ mm., from which thickness it will be observed that if we correct for reflection, white fluorite is perfectly transparent, while the green variety is likewise beyond 2.5 μ. This transparency has been observed by Rubens and others, and continues beyond 6 μ, where it decreases to zero at 10 μ.

From the curves it will be seen that for certain work on radiation the green fluorites are just as serviceable as white ones, which latter are becoming difficult to obtain.

ROCK SALT (NaCl).

($t = 3.11$ mm. Fig. 57.)

The surfaces of this cleavage section were slightly blurred from moisture, and the curve is given to show its great effect in the visible spectrum, which becomes negligible in the infra-red.

CALCITE ($CaCO_3$).

($t = 0.14$ mm.; cut 70° to axis. Curve *a*, fig. 58.)

The section used was a small piece, 5 by 6 mm., made for polarimetric work. It was too short to cover the whole slit, hence the actual trans-

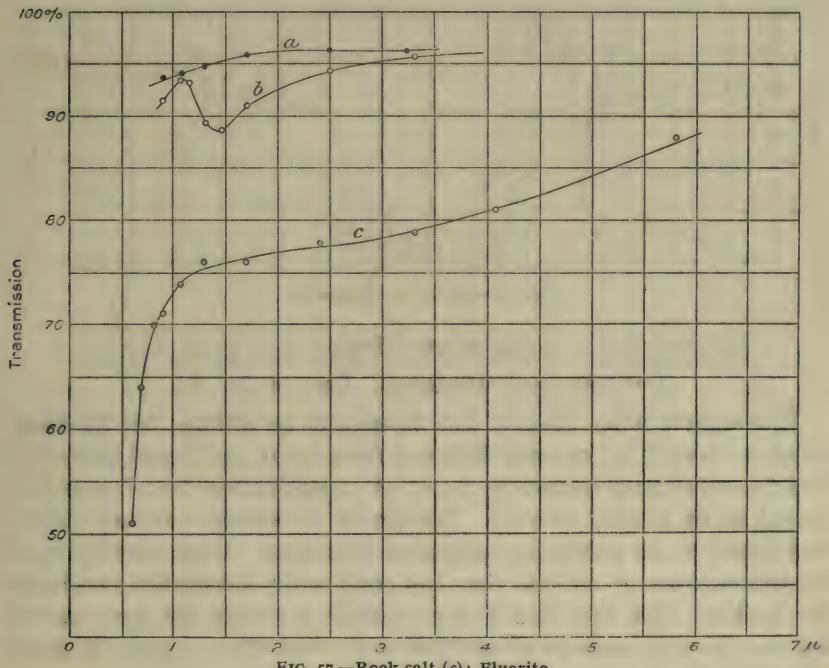

FIG. 57.—Rock salt (*c*); Fluorite.

mission is greater than 55 per cent, indicated on the curve. The curve is remarkable for its transmission of heat-waves. After passing through the opaque region at 7 μ, the section is again fairly transparent to 14 μ. There are bands at 3.44, 3.93, 4.6, 5.7, 6.5 to 7.5, 8.5, 9.4, 10, 10.7, 11.3, 12.2, 12.5, and 13.2 μ. The region of great absorption at 3.4 to 3.9, 6.5 to 7.5, and 15 μ are closely harmonic.

It will be noticed that the CO_2 band at 4.28 is lacking, while the 4.6 μ band, found in CO, is small, from which it appears that CO_2, which is

so prominent as a gas, is differently bonded in calcite and magnesite. The same thing has been noticed in Azurite.

MAGNESITE ($MgCO_3$).

(Massive; subtranslucent; $t = 0.09$. Curve *b*, fig. 58.)

This mineral is more unusual than calcite. It has the transparent region of calcite, at 5 μ, preceded and followed by almost complete opacity. The bands at 3.3 and 3.8 μ are probably in common with calcite.

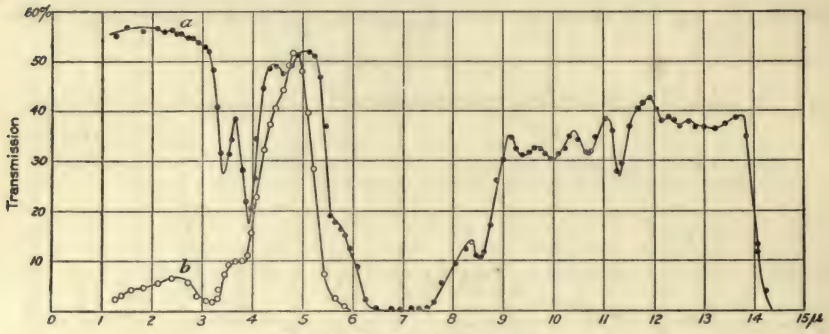

FIG. 58.—Calcite (*a*); Magnesite.

CASSITERITE (SnO_2).

($t = 0.085$ mm.; transparent. Curve *a*, fig. 17.)

This section, when bought, was thought to be mellite; but its transmission curve is so entirely different from what one would expect to find for substances containing water of crystallization that it was suspected to be another mineral. Specimens of mellite were purchased, and found to be unusually opaque to heat rays. Upon inquiry from the maker it was found that they had accidentally substituted cassiterite for mellite. The fact that it was possible to detect the error would indicate that the method of analysis is trustworthy. There are small absorption bands at 1.3, 3, 5.8, 6.6, 7.3, 8.25, 9.7, and 10.4 μ.

PART IV

INFRA-RED REFLECTION SPECTRA

CHAPTER I.

INTRODUCTION.

Previous work on this subject has been rather disconnected, and the present investigation is only preliminary to an extended inquiry into the subject. Nichols[1] compared the reflecting power of quartz with silver, and found that from the visible to 8 μ only a small amount is reflected, while at 8.5 and 9.02 μ there are two intense reflection bands which have a reflecting power almost as great as silver. This work was continued by Rubens and Nichols,[2] by using successive reflections from several surfaces of the same mineral, who found the location of the maxima of the selectively reflected rays ("Reststrahlen") of a series of substances, including quartz, mica, rock salt, sylvite, crown and flint glass, sulphur, alum, and calcite. By using a wire grating they were able to extend their observations to 61 μ, the longest heat-waves yet discovered.

In 1900, Aschkinass,[3] using a rock-salt prism, compared the reflecting power of a series of minerals, including marble, calcite, selenite, and alum. He found that marble and calcite have strong reflection bands at 6.7 and 11.4 μ, while selenite has a band at 8.69 μ. The 6.67 band of marble is broad, and no doubt complex; and in the present work it will be noticed that the calcite band is also double, with the stronger component at 6.6 μ.

Recently Porter,[4] using the method of Rubens and Nichols, found the selectively reflected rays of a series of compounds for the region extending to 10 μ. By this method he was able to locate maxima which are very small and would not appear by a single reflection. For example, potassium ferrocyanide has a series of medium-sized bands which were found in the present examination of absorption spectra, one of which also appears in his reflection spectrum of this compound.

APPARATUS AND METHODS.

The apparatus for the absorption work was used in the present examination. To this end the Nernst heater was replaced by a sliding carrier containing the reflecting mirrors (fig. 59). The carrier consisted of a vertical sheet of metal which, by means of cords and pulleys, was moved

[1] Nichols: Phys. Rev., 4, p. 297, 1897.
[2] Rubens and Nichols: Ann. der Phys. (3), 60, p. 418, 1897.
[3] Aschkinass: Ann. der Phys. (4), 1, 42, 1900.
[4] Porter: Astrophys. Jour., 22, p. 229, 1905.

back and forth in a horizontal direction in a very accurately milled slot. Two openings, each having an area of 2 by 3 cm., were cut into the sheet of metal, over which and facing the spectrometer slit were attached the mirrors. The silver mirror was, of course, permanently attached over one of the openings in the carrier, and it was a simple matter to attach the previously prepared reflecting surfaces of the minerals over the other opening. This brought the reflecting surfaces of the silver mirror and the mineral into the same plane, and limited the exposed area to the size of the opening in the carrier. The silver mirror was chemically deposited upon a plane glass plate, and was new.

Occasionally the reflecting surface of the mineral was simply a cleavage plane—for example, selenite and celestite.

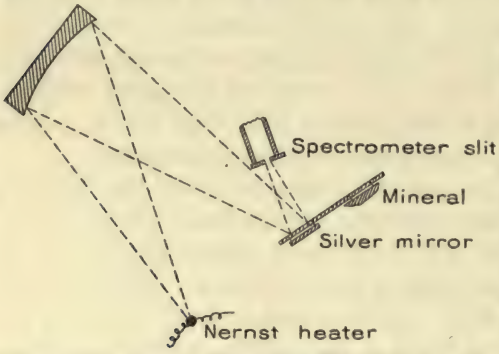

FIG. 59.—Arrangement of apparatus for reflection work. Spectrometer not shown.

The angle of incidence upon the mirrors was 25°. Since we are finding the ratio of the reflecting power of the mineral to that of silver, this large angle, which was unavoidable on account of the construction of the spectrometer, will not affect the results appreciably. The values given are slightly higher than the absolute reflecting power, but the correction is only about 2 per cent[1] at the maximum, and since so much depends upon the condition of the reflecting surface of the mineral, the correction has not been made, except for the metals.

The spectrometer slits were 0.3 mm., or about 2″ of arc, as in the preceding work. The radiation from the Nernst "heater" was thrown upon the reflecting mirrors by means of a mirror having a focal length of 15 cm. and an aperture of 12 cm.

As mentioned elsewhere, in a majority of minerals the general absorption increases so rapidly beyond 5 μ that unless one can reduce the thickness to 0.01 mm. it is impracticable to examine them. It is not a difficult matter to reduce liquid films to this thickness. On the other hand, to grind a solid to even 0.1 mm., and then mount it so that it will be free from glue and free from its support, is not practicable in many cases. The reflection method is not much more advantageous, because larger

[1] Hagen and Rubens: Ann. der Phys. (4), 11, 873, 1903, have found the reflecting power of silver to be about 98.5 per cent throughout the spectrum beyond 2 μ.

surfaces will be required. Hence the present examination is limited to those minerals which afforded surfaces 1 by 2 cm. or larger.

Before discussing the results it will be well to recall some of the known facts in regard to absorption, reflection, and dispersion. In case of normal dispersion the index of refraction decreases with increase in wave-length. For a transparent substance this means a decrease in reflecting power, with increase in wave-length. In the region of an absorption band the refractive index will be abnormally decreased on the side toward the short wave-lengths, while it will be abnormally increased on the side of the long wave-lengths. Consequently the reflection curve, which is now a function of the refractive index and the extinction coefficient, will be abnormally decreased on the side of short wave-lengths and abnormally increased on the side of the long wave-lengths.

These facts are well illustrated in the present series of curves. The same is to be observed in Aschkinass's curves. He makes no comments, however, although the minerals were examined in connection with the question of anomalous dispersion. In comparing the present curves with the transmission curves it will be noticed that the maxima do not coincide. This is to be expected, for in the transmission curves in the region of great absorption and anomalous dispersion the loss of energy is mostly by reflection, hence the maximum will be abnormally broadened and shifted. This is well illustrated in the transmission curve of potassium nitrate, which has a large opaque region extending from 6.5 to 8.5 μ. Before examining this region by reflection the writer expected to find this region to be a complex of several bands, as in calcite, or at least of one large band with a maximum at about 7.5 μ. The reflection band, however, is found at 7.18 μ, and the asymmetry in the transmission curve is to be attributed to the slight loss of energy, by reflection on the side of the short wave-lengths and to a correspondingly great loss on the side of the long wave-lengths.

Before discussing the reflection curves it may be added that the crystalline minerals were usually cleavage pieces cut (but not always polished) in the same direction as for the transmission work. A series of sulphates will first be noticed.

CHAPTER II.

INFRA-RED REFLECTION SPECTRA OF VARIOUS SUBSTANCES.

SULPHATES.

Selenite ($CaSO_4+H_2O$).

Cleavage piece[1] cut parallel to *b* axis. The curve *a*, fig. 60, shows a uniform decrease in reflection to 7 μ, then an abnormal decrease to 7.8 μ. The maximum occurs at 8.7 μ (Aschkinass, 8.69 μ), and from its lack of symmetry may be complex. In fact, from what follows one would

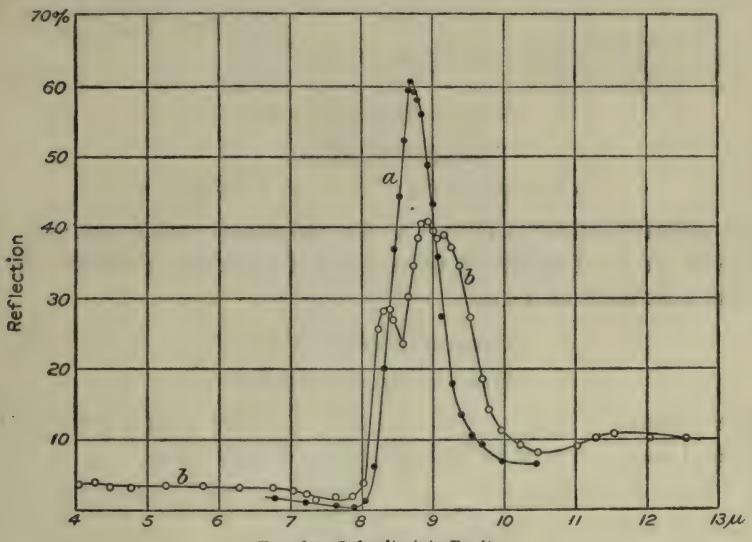

Fig. 60.—Selenite (*a*); Barite.

expect another band at 9.1 μ, which is of frequent occurrence, and is harmonic with the SO_4 band at 4.5 μ.

In a recent research by Koch,[2] who used a reflection band as a source of energy in an interferometer, there are indications that the band of selenite at 8.7 μ is complex.

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[1] In the present discussion "cleavage piece" signifies that the natural unpolished surface was used.

[2] Koch: Ann. der Phys. (4), 17, p. 658, 1905.

BARITE ($BaSO_4$).

(Massive. Curve *b*, fig. 60.)

The reflection decreases normally from 4 to 6.8 μ, then abnormally to 7.8 μ. There are maxima at 8.35, 8.9, and 9.1 μ, followed by a transparent region to 12 μ, where the present observations cease. The reflection appears to increase at 11.5 μ.

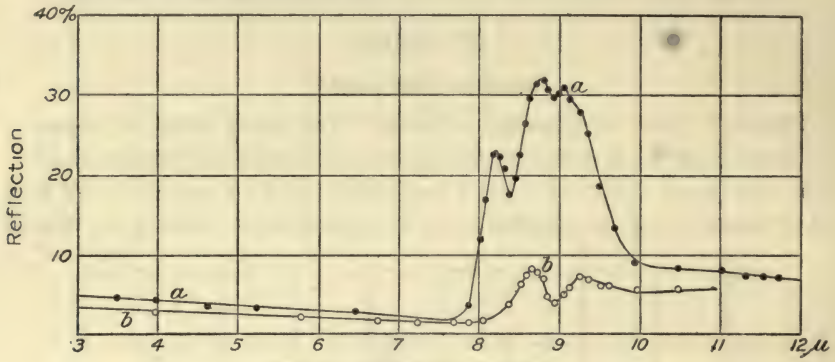

FIG. 61.—Celestite (*a*); Kieserite.

CELESTITE ($SrSO_4$).

(Cleavage parallel to *c*. Curve *a*, fig. 61.)

The reflection curve is similar to the preceding, with maxima at 8.2, 8.76, and 9.1 μ. The region beyond 9 μ is evidently complex, with a possible maximum at 9.3 μ.

KIESERITE ($MgSO_4+2H_2O$).

(Massive. Curve *b*, fig. 61.)

This mineral is hydroscopic, and does not take a high polish. The two small maxima occur at 8.7 and 9.25 μ, respectively.

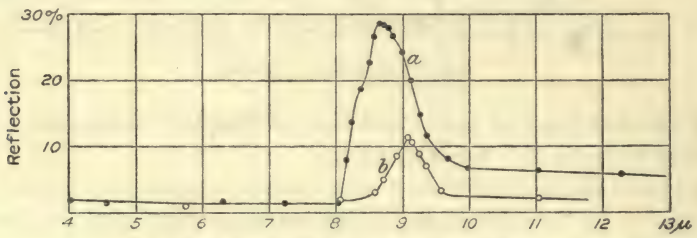

FIG. 62.—Glauberite (*a*); Ferrous sulphate.

GLAUBERITE ($NaSO_4CaSO_4$).

(Ground parallel to *c*. Curve *a*, fig. 62.)

The maxima in this curve are not well defined, particularly the one at 9.1 μ and the one at 8.3 μ. The band at 8.7 μ is not so sharp as in selenite.

FERROUS SULPHATE ($FeSO_4+7H_2O$).

(Curve *b*, fig. 62.)

This crystal dehydrated so rapidly that the surface became rough. There is one well-defined maximum at 9.1 μ which is harmonic with the SO_4 band at 4.55 μ.

ALUM ($K_2SO_4Al_2(SO_4)_3+24H_2O$).

(Curve *a*, fig. 63.)

Aschkinass (loc. cit.) found a small reflection band at 9.05 μ. The present examination was made to compare it with that of other compounds having the SO_4 radical. The maximum was found at 9.1 μ.

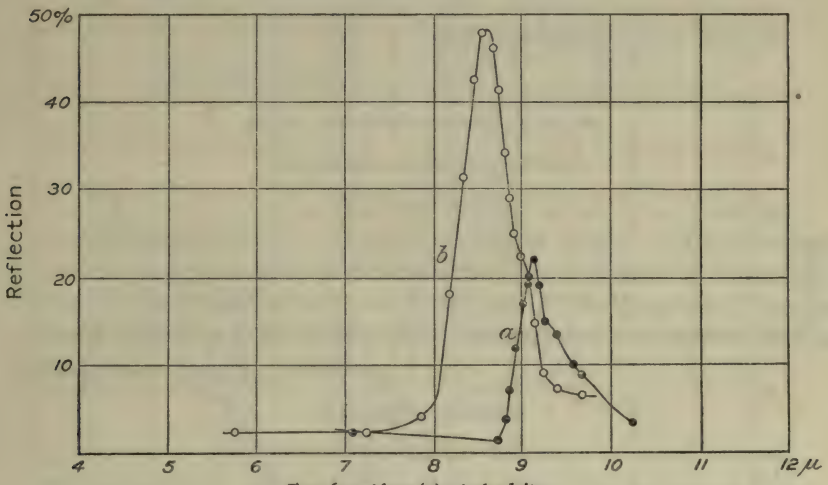

FIG. 63.—Alum (*a*); Anhydrite.

ANHYDRITE ($CaSO_4$).

(Curve *b*, fig. 63.)

Cleavage pieces pasted upon cardboard to form an area sufficiently large for reflection. In comparison with selenite, it will be noticed that the large maximum of the latter is here found at 8.6 μ, followed by a small band at 9.1 μ. It seems a little surprising that the latter band should be so small if it is a harmonic of the large band (of $CaSO_4$) at 4.55 μ.

DIASPORE, AlO(OH).

(Cleavage piece parallel to *b*. Curve *a*, fig. 64.)

This is the most remarkable mineral yet examined. For the region up to 8 μ it has no marked absorption bands. Beyond this point conditions are entirely reversed. There is a broad reflection band extending

from 9.4 to 10.3 μ, with maxima at 9.45, 9.8, and 10.2 μ. The region from 12 to 13 μ is complex, with a maximum at 12.8 μ. In addition to this are sharp maxima at 8.55, 13.8, and 14.6 μ.

Quartz (SiO_2).

(Curve *b*, fig. 64.)

Section cut perpendicular to optic axis. The examination was made to compare the maxima of the silicates studied. The maxima (at 8.48 and 9.02 μ) agree well with those found by Rubens and Nichols, using a wire grating. The enormous reflecting power of 95 per cent at 9 μ

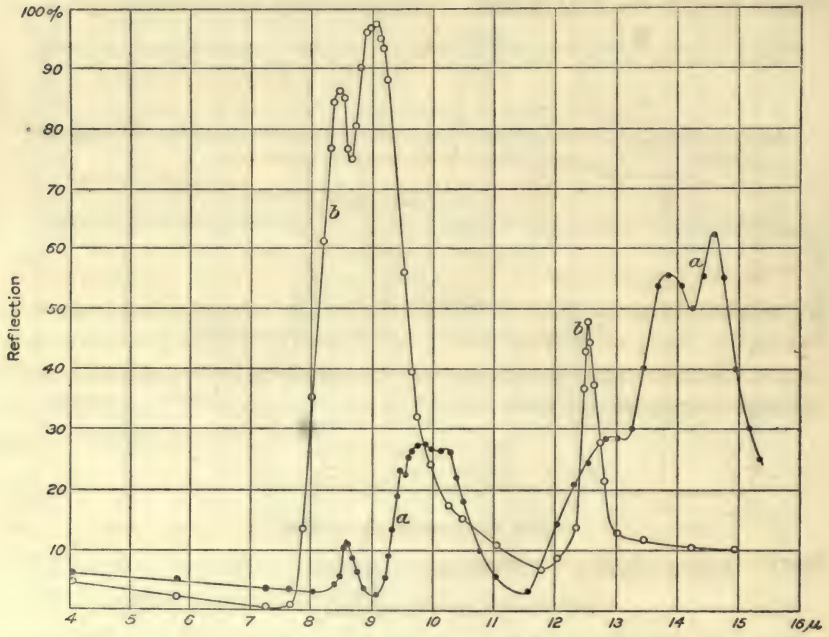

FIG. 64.—Diaspore (*a*); Quartz.

has been found only in quartz, and is slightly higher than found by others. In the silicates to be noticed presently it will be found that the bands found in quartz are shifted to new positions for each new compound examined.

A new band which is unusually sharp and narrow was found at 12.5 μ. It is so very narrow that it seems more appropriate to call it a line instead of a band.

Trowbridge measured the reflecting power of quartz at 9, 10, 11, 12, and 12.78 μ, and found a rapid decrease to 12 μ, while the last reading is much higher, which increase he interpreted as being due to the band at

20.75 μ. From the present curves, which include more observations in the same region, it will be noticed that his last observation was in the midst of a reflection band, beyond which the reflecting power decreases to a low value as it approaches the 20.75 μ band.

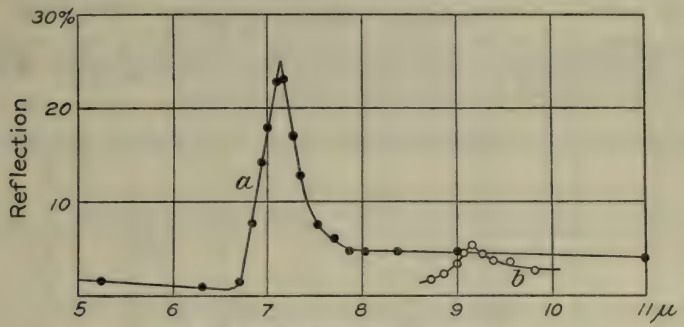

FIG. 65.—Potassium nitrate (*a*); Enstatite.

POTASSIUM NITRATE (KNO_3).

(Curve *a*, fig. 65.)

This compound shows a sharp maximum at 7.15 μ. As was noticed elsewhere, the great shift of this maximum, as compared with the band formed in the transmission curve, is due entirely to the great difference in the reflection on both sides of the transmission curve, which is given without correction for reflection.

ENSTATITE ($MgSiO_3$).

(Curve *b*, fig. 65.)

This mineral is a mass of fine crystals. The reflecting power is low; there is a small maximum at 9.1 μ.

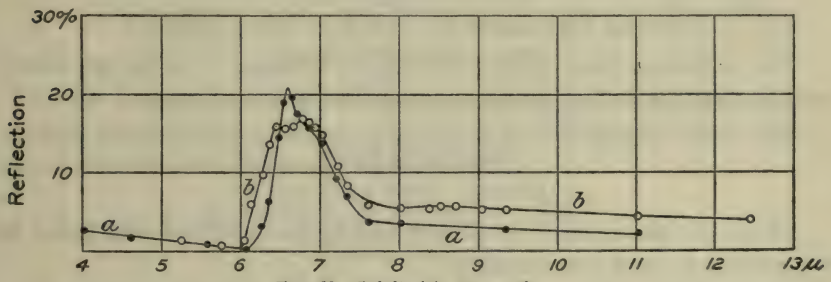

FIG. 66.—Calcite (*a*); Magnesite.

CALCITE ($CaCO_3$).

(Curve *a*, fig. 66.)

Reflection from a natural cleavage face of Iceland spar. The transmission curve shows a wide complex band extending from 6 to 8 μ.

The reflection is complex, with maxima at 6.6 and 6.85 μ. Aschkinass[1] found a band at 6.69 μ for Iceland spar, while his curve for marble is flat, and evidently complex.

MAGNESITE ($MgCO_3$).

(Massive. Curve *b*, fig. 66.)

The band of selective reflection is similar to that of calcite, and consists of two maxima at 6.5 and 6.8 μ, respectively.

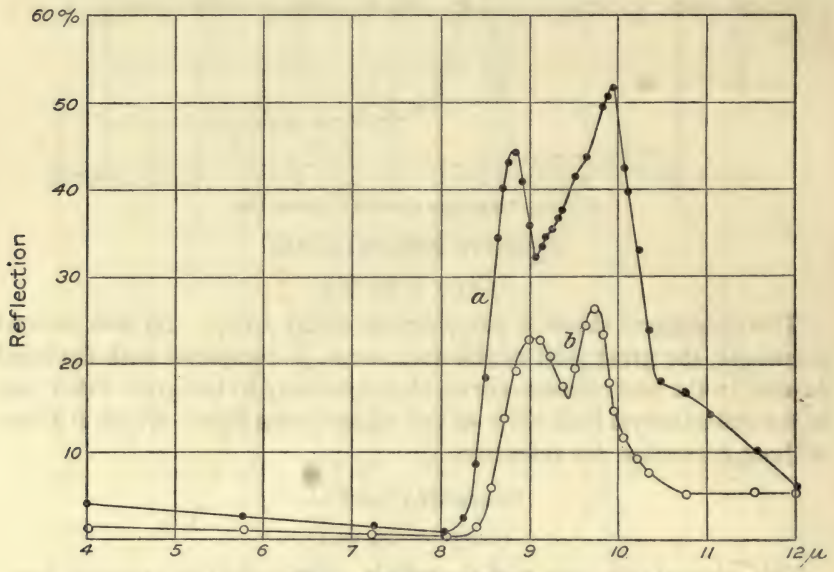

FIG. 67.—Microcline (*a*); Talc.

MICROCLINE ($KAlSi_3O_8$).

(Cleavage piece parallel to *c*; polished. Curve *a*, fig. 67.)

The reflection band from 9 to 10 μ is complex. There are sharp maxima at 8.85 and 9.95 μ, with a probable band at 11 μ.

TALC ($H_2Mg_3Si_4O_{12}$).

(Massive. Curve *b*, fig. 67.)

There are sharp maxima at 9.05 and 9.75 μ. Beyond this point to 12 μ there is great transparency.

[1] Aschkinass, loc. cit.

MUSCOVITE MICA ($H_2KAl_3(SiO_4)_3$).

(Curve *a*, fig. 68.)

Cleavage piece, clear white; a thick piece shows a slight brownish color. The micas are the only minerals examined in which the maxima do not agree with those found by previous observers. From the fact that quartz was examined at the same time, and no disagreement was observed with other observers, the discrepancy is probably due to the kind of mica used.

Rubens and Nichols (loc. cit.) found reflection bands at 8.32 and 9.38 μ.

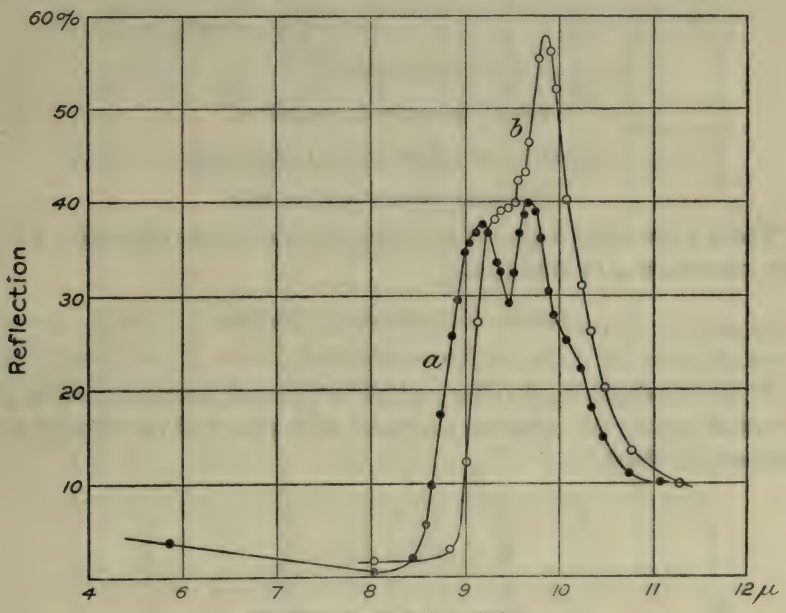

FIG. 68.—Muscovite (*a*); Biotite.

In the present curve there are bands at 9.2, 9.7, and 10.2 μ. The absence of the 8.32 μ band was also noted by Rosenthal,[1] whose reflection curve does not show any sharp maxima.

BIOTITE MICA, $(H,K)_2(Mg,Fe)_2Al(SiO_4)_3$.

(Curve *b*, fig. 68.)

The biotite curve has maxima at 9.3, 9.6, and 9.85 μ, the latter being unusually sharp. The reflecting power of the micas is high in comparison with some of the silicates. The position of the maxima is variable,

[1] Rosenthal: Ann. der Phys. (3), 68, p. 791, 1899.

and is no doubt to be attributed to the variable composition of the mineral.

DEWEYLITE ($H_4Mg_4(SiO_4)_3+4H_2O$).

(Curve *a*, fig. 69.)

This mineral has a complex region of selective reflection extending from 9.5 to 11 μ. There are maxima at 9.65 and 10.5 μ.

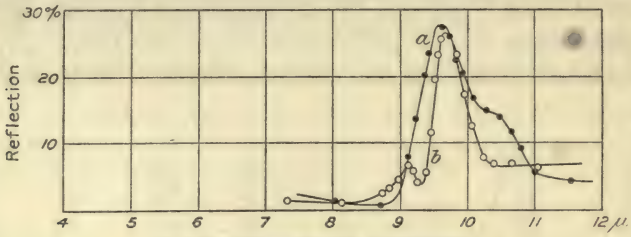

FIG. 69.—Deweylite (*a*); Apophyllite.

APOPHYLLITE ($H_7KCa_4(SiO_4)_3+4\frac{1}{2}H_2O$).

(Cleavage parallel to *c*, fig. 69.)

There is the usual region of reflection common to the silicates. There are maxima at 9.15 and 9.7 μ.

SODIUM METAPHOSPHATE ($NaPO_3$).

(Curve *a*, fig. 70.)

There is a single band at 8.0 μ which is harmonic with the band at 4 μ. In other regions the reflection compares with glass and the vitreous substances examined.

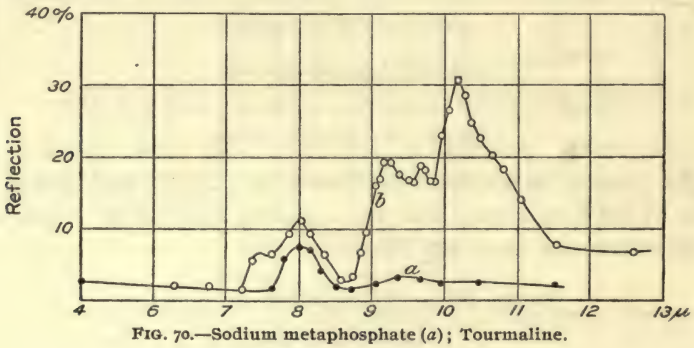

FIG. 70.—Sodium metaphosphate (*a*); Tourmaline.

TOURMALINE ($H_8Na_2Fe_4B_6Al_3Si_{12}O_{62}$).

(Curve *b*, fig. 70.)

The reflection was formed from a natural crystal face. There are maxima at 7.5, 8.0, 9.2, 9.7, 10.2, and 10.7 μ.

SERPENTINE ($H_4(Mg,Fe)_3SiO_9$).

(Curve *a*, fig. 71.)

The reflecting power of this mineral is low. The maxima are at 9.7 and 10.5 μ.

COLEMANITE ($Ca_2B_6O_{11}+5H_2O$).

(Cleavage piece parallel to *b*. Curve *b*, fig. 71.)

From the transmission curve it will be noticed that this mineral is very opaque. Yet it has no metallic reflection bands before arriving at 7 μ. Its reflecting power of only 1 per cent at 4 μ is unusually low. There are maxima at 7.3, 7.6 (?), 9.4, 10.6, and 11.2 μ.

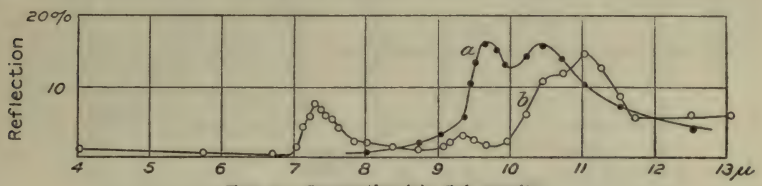

FIG. 71.—Serpentine (*a*); Colemanite.

ALBITE ($NaAlSi_3O_8$).

(Curve *a*, fig. 72.)

Section ground parallel to a cleavage plane. The curves of soda and potash feldspars are unusually similar, as was found for transmission. The maxima occur at 8.7, 9.7, and 10 μ.

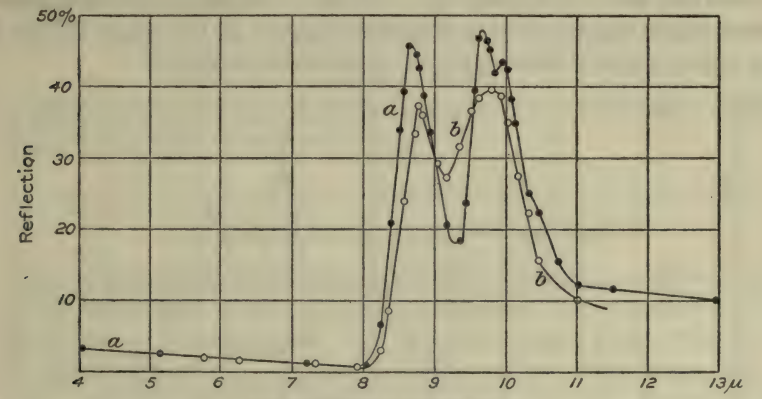

FIG. 72.—Albite (*a*); Orthoclase.

ORTHOCLASE (var. ADULARIA) ($KAlSi_3O_8$).

(Curve *b*, fig. 72; cleavage parallel to *c*.)

The first maximum is shifted to 8.8 μ, while the second is a broad band, with a maximum at 9.8 μ.

AMPHIBOLE ($CaMg_3(SiO_3)_4$).

(Curve *a*, fig. 73.)

The general trend of the reflection curve is similar to quartz. There are maxima at 8.7, 9.45, 10.03, and 11 μ, the first and last being small and not well defined.

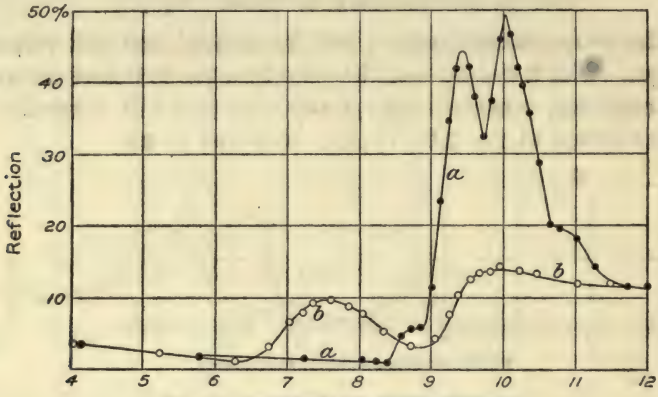

FIG. 73.—Amphibole (*a*); Sodium biborate.

SODIUM BIBORATE ($Na_2Br_4O_7$).

(Curve *b*, fig. 73.)

This substance is a glass made by fusing borax. The surface was well polished; nevertheless the reflection bands are weak. The maxima are wide and occur at 7.5 and 10 μ. From a comparison with the transmission curve it appears that the great opacity of this glass is due to some other property than to bands of selective reflection.

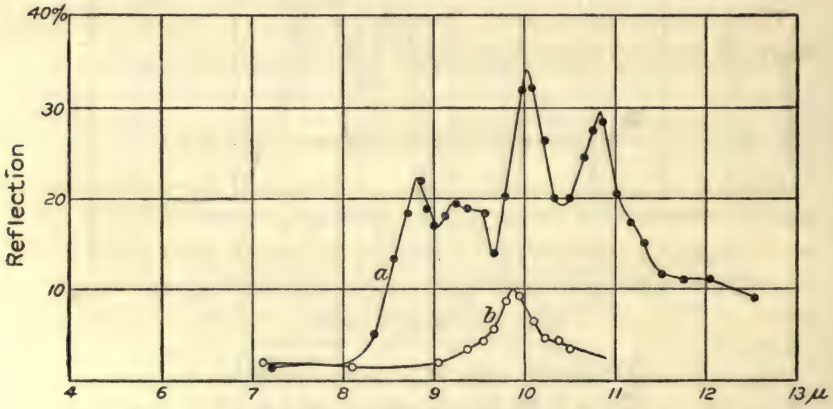

FIG. 74.—Datolite (*a*); Hydrotalcite.

DATOLITE ($Ca(BOH)SiO_4$).

(Curve *a*, fig. 74.)

The reflection curve shows a series of small, sharp maxima at 8.8, 9.2, 9.5, 10, and 10.8 μ. The reflection was from a natural crystal face.

HYDROTALCITE ($Mg_3Al(OH)_8+3H_2O$).

(Curve *b*, fig. 74.)

The results from this mineral are rather disappointing. There is but one reflection maximum at 9.9 μ, and this one is not very large. The transmission curve shows great opacity.

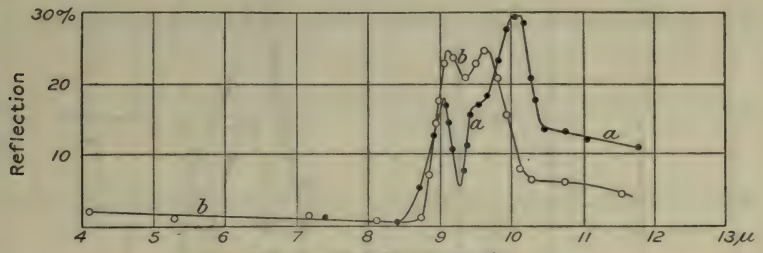

FIG. 75.—Natrolite (*a*); Apatite.

NATROLITE ($Na_2Al_2Si_3O_{10}+H_2O$).

(Curve *a*, fig. 75.)

Reflecting face ground parallel to *m*. There are maxima at 9.05, 9.5, and 10.05 μ, beyond which point the reflecting power remains unusually high to 12 μ.

APATITE ($Ca_5F(PO_4)_3$).

(Curve *b*, fig. 75.)

The reflecting power gradually decreases to 7.5 μ, beyond which point there are maxima at 9.12 and 9.65 μ.

GLASS.

(Curves *a*, *b*, *c*, fig. 76, and curve *a*, fig. 78.)

Glass is of such a variable composition that if the various metallic oxides other than of silicon had an effect upon the reflection bands one would expect to observe it. For example, crown glass O381 contains $68.7SiO_2+13.3PbO+15.7Na_2O+2ZnO$, while a flint silicate S57 contains $21.9SiO_2+78PbO$, and a lead glass contains $4.62PbO+8K_2O+45SiO_2$.

The following samples show that the variation in the silicate content of the glass has little effect upon the maxima, except that of intensity.

The curves show a slight curvature at 8.6 to 8.8 μ, a sharp maximum

at 9.2 to 9.3 μ, and a third band at 9.7 μ. Curve *a*, fig. 76, gives the reflection for a monochromatic red glass, No. 2745, made by Schott & Co., of Jena; curve *b* is for a plane parallel interferometer plate; curve *c* is for a piece of fluorescent uranium glass, while curve *a*, fig. 78, is for a piece of ordinary plate glass.

The fluorescent glass has an unusually low reflecting power. All of the samples have a uniform reflecting power to 7.0 μ, then a sudden decrease, followed at 8 μ by a large band of selective reflection. For

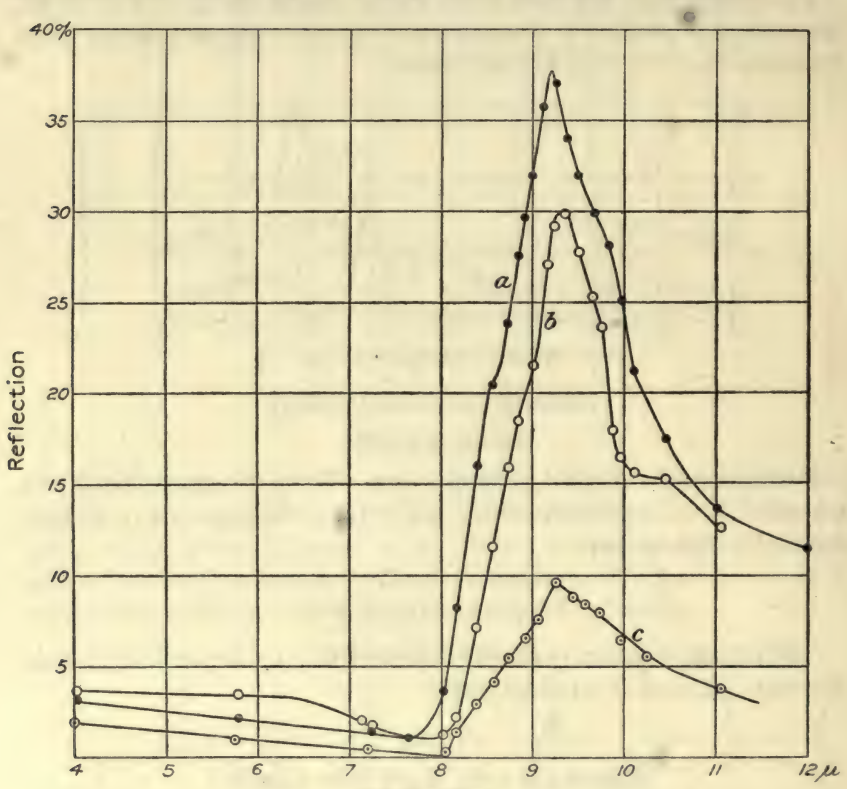

FIG. 76.—Glass.

the transmission curve of glass (fig. 53) it will be noticed that there is a decrease in the transparency beyond 15 μ. Hence one would expect to find the reflection curve to be irregular as observed, being abnormally high just beyond the reflection band at 9.3 μ, and abnormally low on approaching the second large absorptive band which lies beyond 15 μ. The glass plates were from 3 to 8 mm. thick, hence opaque beyond 4 μ, so that the reflection values are not influenced by energy reflected from the second surface, *i. e.*, the reflection is from only one surface.

Pfund[1] has published a reflection curve of glass, which is entirely lacking in these small bands, due to the fact that only six spectrometer settings were made between 8 and 12 μ, while nineteen settings were made in the present work.

Granite.

(From Barre, Vermont. Fig. 77.)

Granite is a mixture of quartz, feldspar, and mica, and hence gives a reflection spectrum which is the composite of these minerals. In the present specimen the mica plates were partly broken off the surface in polishing.

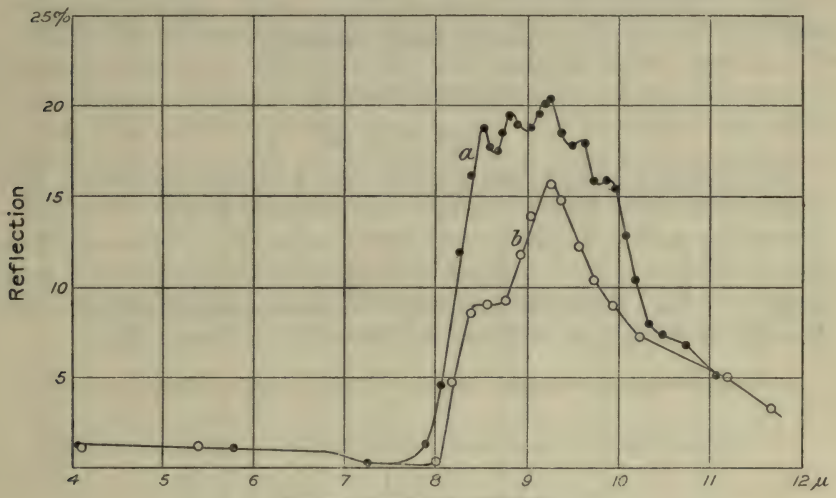

Fig. 77.—Granite (*a*); Porcelain.

Porcelain (Glazed).

(Curve *b*, fig. 77.)

The specimen was a flat fragment of a glazed white porcelain dish. As is well known, porcelain ware is made from kaolin, which is the decomposition product of aluminous minerals, especially the feldspar of granitic rocks.

The reflection curve shows maxima at 8.5 and 9.25 μ.

Pectolite ($HNaCa_2(SiO_3)_3$).

(Curve *b*, fig. 78.)

The specimen examined was spindle-shaped, consisting of two masses of needle-shaped crystals grown end to end. The reflecting surface

[1] Pfund: Astrophys. Jour., 24, p. 25, 1906.

was ground parallel to the needles. The reflection curve is of the usual form and shows maxima at 9.4, 10.3, and 10.8 μ.

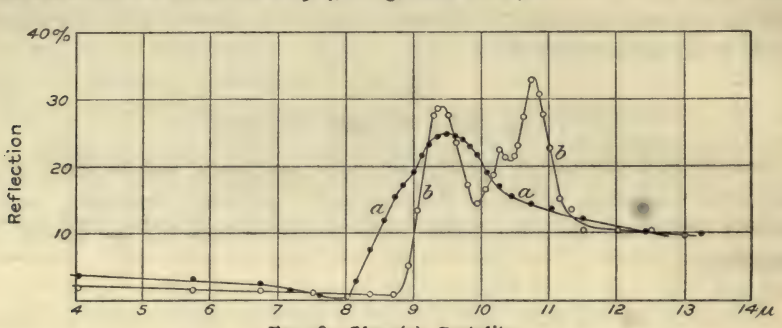

FIG. 78.—Glass (*a*); Pectolite.

WILLEMITE (Zn_2SiO_4).

(Curve *a*, fig. 79.)

The reflecting surface was ground from a massive specimen. The transmission curve becomes opaque very abruptly at 9 μ. This is followed by a sudden rise in the reflection curve at 10 μ. There are three strong maxima at 10.1, 10.6, and 11 μ, respectively, followed by a small band at 11.6 μ. From the location of the maxima it is evident that the bonding of the SiO_2 in willemite is different from that of quartz.

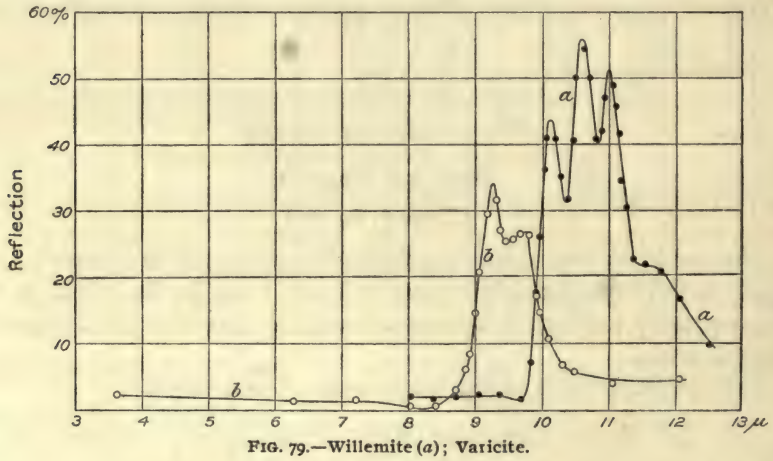

FIG. 79.—Willemite (*a*); Varicite.

VARICITE ($AlPO_4+2H_2O$).

(Curve *b*, fig. 79.)

The reflecting power is low, and decreases uniformly from 4 to 7.5 μ, where it decreases abruptly to 8.5 μ. There are maxima at 9.25 and

9.7 μ. The latter is not very well defined, so that, from the fact that it coincides with a band found in apatite, one can hardly infer that it is due to the PO_4 radical.

SULPHIDES.

Stibnite (Sb_2S_3).

(Large fresh cleavage piece parallel to *b*, perfectly plane without striations. Area 1 by 1.5 cm. Curve *a*, fig. 80.)

The reflecting power of the sulphides of Zn, Pb, Fe, and Sb are worthy of notice. They are known for their metallic luster, especially stibnite (Sb_2S_3). Their reflecting power in the infra-red is equally conspicuous for its high value, which is uniform throughout the region examined to 12 μ. Stibnite is the most marked in this respect. By transmission it was found to be unusually transparent, the absorption of a thin film, 0.45 mm., being about 45 per cent throughout the whole region to 12 μ, beyond which there appears to be another absorption band. The reflecting power was found to be about 35 per cent to 11 μ,

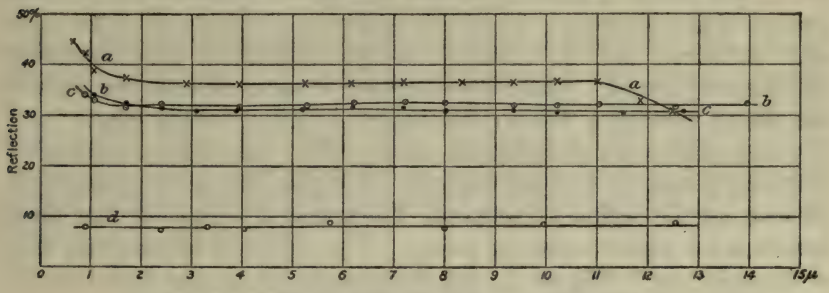

Fig. 80.—Stilbite (*a*); Pyrite (*b*); Galena (*c*); Sphalerite (*d*).

so that after eliminating the reflection the mineral is almost transparent. This is well illustrated in curve *b*, fig. 55, which is for a section 10 times that for curve *a*. It will be noticed the true absorption is only about 5 per cent. It is difficult to decide from the present date whether the band beyond 14 μ is due to absorption or to selective reflection. The reflection curve drops in the region of 13 μ, which would indicate a selective reflection just beyond this point.

The observations were repeated on different specimens, and no difference greater than experimental errors was found in the reflecting power, so that it can be definitely stated that the reflecting power is higher in the visible spectrum, and drops to a lower value beyond 12 μ. This, as well as the other sulphides, was found to be opaque to Roentgen rays.

The refractive index of stibnite, found by Drude, for sodium light is 4.49 (5.17).

The value calculated from the well-known Fresnel formula:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

for the region from 4 to 8 μ, where the reflecting power is $R = 36$, $n = 4.0$, and $n^2 = 16$. The dielectric constant, determined for me by Dr. N. E. Dorsey by the static method, by placing thin sections in a small air condenser, is about 8 to 9, which is only about one-half the computed value, $\epsilon = n^2 = 16$.

The difference is so great that it is not permissible to consider this substance a transparent non-conductor. Of course, if there is a large reflection band beyond 15 μ (fig. 55) the above assumption is not true. The proper test would be to find the reflecting power for Hertz waves.

Königsberger and Reichenheim[1] examined a series of natural sulphides by means of what may be called spectrum energy screens or filters, viz, plates of quartz, fluorite, etc., which transmit only certain regions of the spectrum. From the thickness of the plates of the minerals examined and the observed energy transmitted they computed the reflecting power. The method can not be as accurate as the present one, which involves a direct measurement of the reflecting power; and this may account for their higher values. For stibnite they observed a reflecting power of 47.6 per cent for the region 0.5 to 4.0 μ, and 43.9 per cent for the region 1.6 to 4.0 μ. Of course, it is possible that their sample had a higher reflecting power. The electrical conductivity was of the order 10^{-15} (Hg = 1), and they concluded, as was found in the present work, that the Maxwell relation does not hold true.

Pyrite (FeS_2).

(From Rio Marina, Island of Elba. Curve *b*, fig. 80.)

The reflecting surface of one specimen was formed by grinding a large crystal face, which was found would not take a high polish. This specimen gradually increased in reflecting power from 25 per cent at 2 μ to 34 per cent at 12 μ. The low reflection at 2 μ is evidently due to lack of polish.

Curve *b* is for a natural cubical crystal face which was 1 by 1.3 cm. in area. It was quite plane, and had a high polish, except at one end, where there were a few striations. A perfect crystal would have a

[1] Königsberger and Reichenheim: Centralblatt für Mineralogie, Jahrg. 1905, p. 465.

slightly higher reflecting power. The specimen has a slightly higher reflecting power in the visible, and beyond 3 μ a constant reflecting power of about 32 per cent[1] to 14 μ.

According to Reichenheim,[2] the electrical conductivity is variable for different specimens on account of impurities, so that no comparisons can be made with the computed reflecting power, such as have been made by Hagen and Rubens[3] for metals.

GALENA (PbS).

(Cleavage piece, surface 2 by 2.5 cm.; quite plane. Curve *c*, fig. 80.)

The reflecting power appears to be slightly higher in the visible than in the infra-red, where it is constant at 31 per cent to 14 μ. No doubt the reflecting power would be slightly higher for a perfect specimen. It was found impossible to grind a surface that was not full of small depressions, due to chipping of the surface.

SPHALERITE (ZnS).

(Curve *d*, fig. 80.)

The specimen examined was a dark mass of crystals. The surface showed several cracks. The reflecting power is no doubt low, even for a perfect surface, as will be noticed from its uniformity throughout the spectrum to 15 μ. No large, clear specimen of this material was obtainable. The refractive index in the visible is 2.369 (Na), while computing from the reflecting power at 5 to 10 μ would indicate a value of $n = 1.85$ for $R = 0.09$.

SULPHUR (S).

(Reflection from large crystal face. Curve *b*, fig. 81.)

The reflection curve is low and uniform throughout the spectrum. It is interesting to note that the absorption bands at 8 and 12 μ (found in a previous examination) are too small to affect the reflection curve. In this connection it will be noticed that all the sulphides examined, except ZnS, have a much higher reflecting power, while the zinc sulphide reflection is practically the same as that of pure sulphur.

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[1] Königsberger and Reichenheim: Centralblatt für Mineralogie, Jahrg. 1905, p. 465, "by extrapolation from the curve for the visible spectrum found a reflecting power of 30 per cent."

[2] Reichenheim: Inaug. Diss., Freiburg, 1906.

[3] Hagen and Rubens: Ann. de Phys. (4), 11, p. 873, 1903.

Carborundum (Silicium Carbide) (SiC).

(Large hexagonal plate, naturally highly polished. Curve *a*, fig. 81.)

This is an artificial product obtained from a carborundum furnace.

The reflection curve is the most remarkable one yet discovered. The selective reflection bands of quartz at 8.5 to 9.03 μ stand second in the order of intensity.

Since absorption, reflection, and refraction are intimately connected, the reflection curve gives us an idea, qualitatively, of the dispersion of this mineral. It will be noticed that the reflection curve drops abruptly from a fairly constant value at 9 μ to a very low value at 10 μ, while beyond 13 μ it remains abnormally high. This is exactly what is found for the refraction curve, in the region of anomalous dispersion, and to illustrate this point the carborundum curve is the best example yet observed. In this connection it will be noticed the reflection curve of quartz decreases more uniformly throughout this whole region.

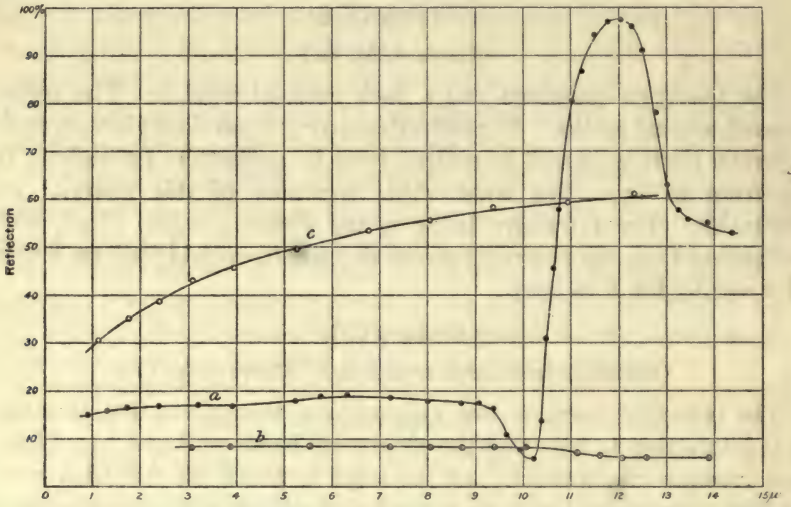

Fig. 81.—Carborundum (*a*); Sulphur (*b*); Graphite (*c*).

Graphite (C).

(Natural mineral from Siberia. Curve *c*, fig. 81.)

The reflecting power of various forms of carbon, such as "gas-carbon" and anthracite, have been examined by Aschkinass,[1] who found the reflection to increase from 30 per cent at 8 μ to 53 per cent at 26 μ for the former, and a uniform reflection of about 13 per cent throughout this same region for the latter.

[1] Aschkinass: Ann. der Phys. (4), 18, p. 373, 1905.

The present sample, which had a high polish, increases uniformly in reflecting power from 40 per cent at 2.5 μ to 60 per cent at 12 μ. It thus appears that the presence of silicon in carborundum lowers the reflecting power up to 9, beyond which it becomes abnormally high.

The results obtained from the present examination of reflection spectra demonstrate a number of important facts. The first one is the dependence of reflection upon absorption. The second point worthy of notice is that the region of selective reflection begins beyond 7 μ, while for the majority of substances studied the region of greatest activity is from 8 to 10 μ. Whether this coincidence in the grouping of reflection bands (of minerals other than those containing SiO_2) is fortuitous is unknown. A knowledge of their dielectric constants might aid in deciding this point. In considering this question of the selective reflection beyond 7 μ, it will be recalled that the "general absorption" of many substances was found[1] to increase beyond this point.

The results as a whole show that there are not such definite bands, whether found by reflection or by absorption, in the silicates as one would expect. In other words, the silicon radical seems to be differently bonded in each mineral. Possibly there are several radicals—SiO_2, SiO_3, SiO_4—one or more of which are present in each mineral, or even in different specimens of the same mineral. This would explain the lack of constancy of the occurrence of the bands of quartz at 3 μ.

The investigation has added one more radical which has definite absorption bands in the infra-red, viz, SO_4, which has harmonic bands at 4.55 and 9.1 μ.

TRANSPARENCY TO X-RAYS.

The majority of these silicates and sulphides were examined under X-rays, and all but graphite were found to be opaque. Of course, the samples were large, which means that in thin sections, no doubt, many of the silicates would be as transparent as glass.

REFLECTING POWER OF METALS.

The reflection power of various metals and alloys, which can be easily produced in the form of concave mirrors, has been measured by Hagen and Rubens.[2] The list does not include Co, Zn, Cd, Al, Sn, Pd, and Ir, the reflecting power of which in the form of plane mirrors is herewith presented.

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[1] Infra-red Investigations, Washington, 1905.

[2] Hagen and Rubens: Ann. der Phys., 8, p. 1, 1902; 11, p. 873, 1903.

The present list can not, of course, be of practical use, since the surfaces tarnish, but from a theoretical standpoint they are of considerable importance. For example, Hagen and Rubens established relations between the reflecting power and the electrical conductivity of the metals studied. One would, therefore, expect similar relations for closely related metals in the Mendeleef's series.

For example, one would expect the reflecting power of cobalt to be of the same order as that of nickel, and a similar relation between zinc and copper, and palladium and platinum. From the present examination it will be noticed that such a close parallelism exists in all cases where the actual condition of the reflecting surface, *i. e.*, its polish, is negligible. Unfortunately in the present list only zinc and cobalt take a high polish which is quite permanent. Cadmium also takes a high polish, but tarnishes in a day or two. Tin can not be given a high polish; palladium is of a similar nature, while aluminum always retains a hazy white surface. As a result, in the shorter wave-lengths the reflecting power is lower than normal, and rises steadily to 8 or 10 μ, where it assumes a constant value which can no doubt be interpreted as real.

The specimens examined were about 3 by 4 cm. area. They were ground plane, then polished with Vienna lime and stearin oil. The silver mirror was finally prepared by "buffing," and had a fine surface.

An attempt was made to use silver-on-glass mirrors, but even those that transmitted only blue light were found to differ as much as 2 per cent in reflecting power, while the best silver-on-glass mirror reflected about 0.5 per cent less than the one of pure silver at 5 μ to 10 μ. A mirror of pure silver was therefore used as a standard of reference. It consisted of a thick (0.5 mm.) sheet of the pure metal soldered on a heavy plate of brass.

The method of observation consisted in placing the standard silver mirror and the comparison mirror upon the carrier before the spectrometer slit, as in the preceding work, and obtaining the ratio of the deflections. This gives the reflecting power relative to silver, and is slightly higher than the absolute reflecting power, since silver is not a perfect reflector. The absolute reflecting power of the metals, given in Table I, were found by multiplying the relative values by the reflecting power of massive silver, given in the first column of the same table.

The reflecting power of Ni and Pt are quoted from Hagen and Rubens (loc. cit.) to show their close relations with Co, Pd, and Ir, respectively. The angle of incidence was about 25°, and was permissible, since it is well known that the reflecting power increases but slightly up to this angle. Of course, the assumption is tacitly made

here that the change in reflecting power with angle of incidence is the same for all the metals examined, and, since we are finding a ratio, will, therefore, affect alike the numerator and denominator of the fraction. Any error thus introduced could be only a fraction of a per cent, which is as accurate as the variation in the polish of different samples of the same metal will permit. The low reflecting power of most of the metals examined in the region of 1 μ is due more to lack of polish and planeness of surface than to a possible transparent region such as obtains in silver, in the ultra-violet. Palladium is lower in reflecting power than platinum; and it is barely possible that it would have a slightly higher value if a better surface could be produced. The specimen was made by soldering a 0.1 mm. sheet upon a heavy plate of brass.

TABLE I.—REFLECTING POWER OF METALS.

[Absolute values.]

Wave-lengths.	Silver (massive, Hagen and Rubens).	Nickel (massive, Hagen and Rubens).	Cobalt (massive, sheet).	Zinc (cast).	Aluminum (sheet).	Tin (cast).	Palladium (sheet).	Platinum (Hagen and Rubens).	Iridium (massive, sheet).	Cadmium (cast).
μ										
1.06	96 4	72.0	67.5	79 4	73.8	54.0	74.8	72.9	79.4	70.8
1.71	97.3	.....	71.5	91.0	80.8	59.3	79 3	79.5	84.7	85.0
3.05	97 3	88.7	76.7	95.5	88.3	68.6	87.5	88.8	91.4	93.0
3 96	97.7	92.5	80.7	96.2	91.4	71.7	88 1	91.5	93.3	95.2
5.24	97.3	94.7	86 2	97.2	93 8	76.7	90.4	93.5	94.2	95.9
6.75	98.5	94 8	92.7	97.2	95.2	80.3	93 3	95.5	94.7	97.0
8.02	98 8	95 0	94.8	98.0	96.9	83.2	94.7	95.1	94.8	97 8
9 38	98 9	95 6	96 4	98 1	97 4	87.0	95 3	95.4	95 6	98.4
10.49	99 0	95.8	96.8	98 4	96.9	87.0	96.6	95.9	95.8	98.3
12.03	98 9	95 7	96.6	98.3	97.3	86.9	96 5	96.5	96.1	98.2
13.00	99.0	95 6	.....	99.0	.....	.....	.....	96.4	.....	.....

Considerable difficulty was experienced in casting a homogeneous plate of cadmium. Success was finally attained by melting it in a thin copper mold. When cool the mold was torn off and the (1 cm. thick) plate filed and ground plane. In fig. 82 it will be noticed that its reflecting power suddenly rises to a constant value beyond 5 μ.

The sheet of cobalt was about 0.5 mm. thick, and permitted considerable filing and grinding. However, it was found impossible to prepare a surface that was free from pores. This probably explains its deviation in reflecting power from that of nickel, out to 10 μ, where it reflects more than nickel, as it should, since its electrical conductivity is higher.

The aluminum was a sheet of commercial material. It took a high polish. Its reflecting power is unusually high beyond 10 μ, and is known to be practically a perfect reflector for heat waves at 25 μ.

Little can be said concerning tin. It was found impossible to give it a polish, although the melted surface on cooling was very bright. From its electrical conductivity it ought to have a reflecting power of the order of nickel and platinum.

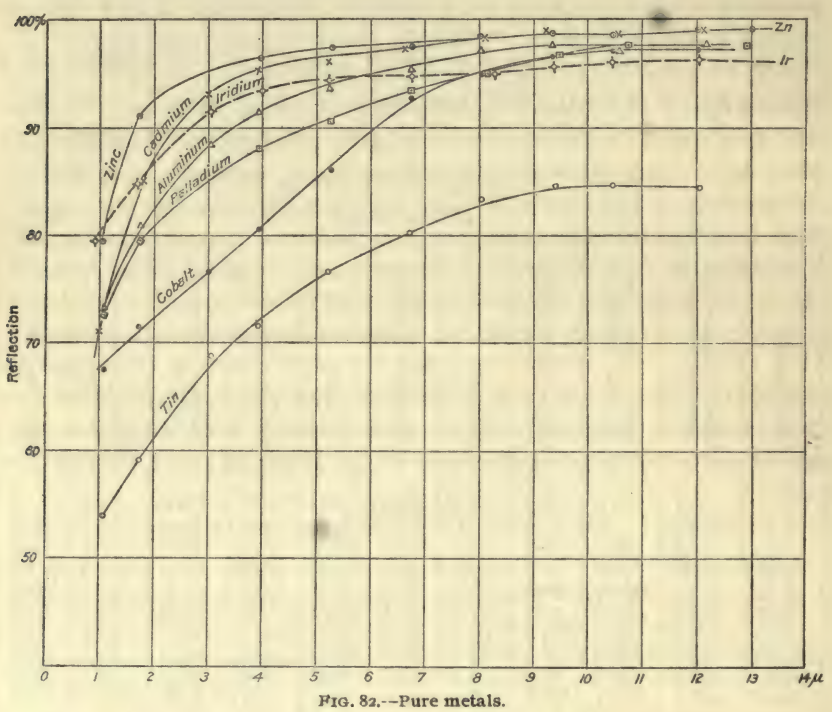

FIG. 82.--Pure metals.

Zinc is the most interesting of all the metals studied. It takes an unusually high polish which is quite permanent. Its color is peculiar. It seems to have a low reflecting power in the visible spectrum, which rises suddenly to a maximum beyond 4 μ, and in this respect compares favorably with silver, which is the highest and most serviceable reflector known for the visible and the infra-red spectrum. The electrical conductivity, as well as the reflecting power, of zinc and of cadmium are close in agreement.

The iridium mirror was obtained by polishing a sheet about 3 by 2 by 0.1 cm. It was not free from scratches, but took a high polish. It has a slightly higher reflecting power than platinum. Its electrical con-

ductivity appears to be unknown, which is also true of the purity of the specimen examined.

The metals, with the exception of aluminum, were obtained from Kahlbaum and from Heraeus. Pure cobalt is, of course, practically unobtainable, and the specimen examined probably contained from 1.5 to 2 per cent nickel.

Hagen and Rubens (loc. cit.) have computed the absorption of the metals from the electrical conductivity by means of the formula $100-R=\frac{36.5}{\sqrt{c\lambda}}$ where R is the reflecting power, c is the reciprocal of the resistance of a conductor 1 m. long and 1 sq. mm. area, in ohms, and λ = wave-lengths in μ = 0.001 mm. They found a slight variation in the observed and computed values of $100-R$, the maximum being about 0.5 per cent at $12\,\mu$. It must be said, however, that if they had selected the wave-length $\lambda = 10.49\,\mu$, where in many cases the value of R is frequently the same as for $12\,\mu$, the discrepancy would be larger, and of the same order as that observed in the present results. In the present work no attempt was made to attain the accuracy of these two investigators, for the reason that the nature of the material would not permit it. The difference in the observed and computed values of $100-R$ is given in the following table, using the values of the electrical conductivity as found by Jager and Diesselhorst.[1]

TABLE II.

Metal.	100—R.	
	Observed.	Computed.
Cd	1.8	2.87
Co	3.4	3.28
Pd	3.5	3.48
Zn	1.7	2.59
Sn	13.	3.55
Al	2.7	1.89

The agreement in the observed and computed values (excepting tin) is as close as one can expect from the nature of the metals examined.

REFLECTING POWER OF SOLUTIONS.

It is well known that in the visible and in the ultra-violet the position of the maximum of absorption of a solid is generally not affected when

[1] Jager and Diesselhorst, quoted in Landolt and Bornstein, Tabellen.

in solution. Stenger[1] found that it is only when a change in the aggregation conditions or in the solving process is accompanied by a change in the physical molecule that a change occurs in the absorption spectrum. One would expect similar conditions in the infra-red. In Appendix IV of the first volume of this investigation a preliminary examination was made of the transmission of several solids in solution, and it was shown that the method is feasible for infra-red work. The present examination by reflection is only preliminary, and was undertaken primarily to learn whether possibly some of the sulphates, which in the solid state have a single sharp maximum at 9.1 μ, really have several bands, say at 8.6 and 9.6 μ, which for some unexplained reason are merged into one. (There seems to be no reason why the sulphates

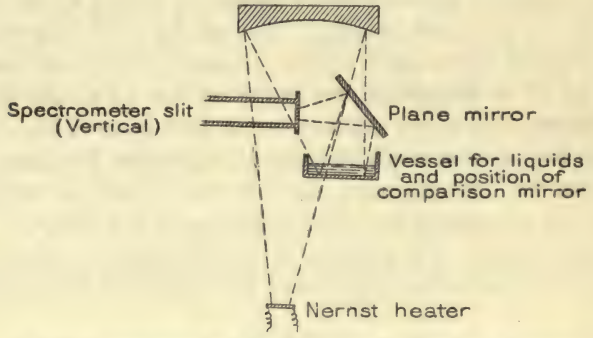

FIG. 83.—Arrangement of apparatus for reflection from solutions.

of Cd, Co, Ni, and Cu should have a single band, while those of Ba, Sr, and Mg should have several bands.) Of course one would hardly expect this to be the case, but preconceived ideas are often deceptive. The constantly recurring bands of the sulphates at 4.5 to 4.6 μ and 9.05 to 9.2 μ reminds one of similar conditions in compounds containing CH_3 groups. The adjustment of the apparatus is shown in fig. 83. On account of the difficulty of adjusting the liquid to the level of the silver comparison surface no attempt was made to obtain the absolute reflecting power accurately.

SULPHURIC ACID (H_2SO_4).

(Concentrated. Fig. 84.)

This substance was not examined for various concentrations, as explained in Appendix II.

The maxima occur at 8.6, 9.55, 10.42, and 11.35 μ. The fact that the 8.6 μ and 9.52 μ band of H_2SO_4 occurs in the hydrous and anhydrous

[1] Stenger: Ann. der Phys. (3), 33, p. 578, 1888.

sulphates examined shows that they are not present exclusively in those sulphates containing water of crystallization. In other words, they are due to the SO_4 radical, and not due to hydrous sulphates, as might be inferred from the study of sulphuric acid. Concentrated sulphuric acid

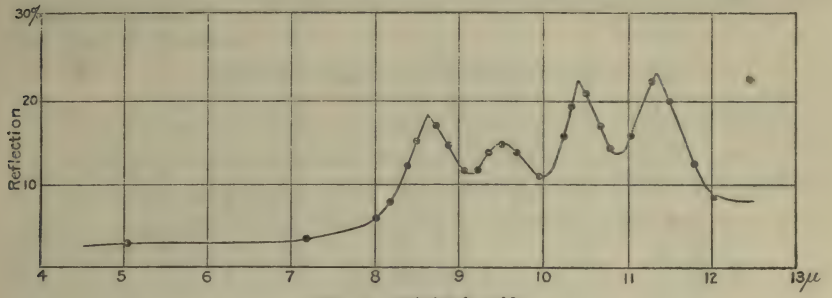

FIG. 84.—Sulphuric acid.

contains SO_3, and it is interesting to note that the 10.4 μ band, which in a previous examination of gases was found in SO_2, is one of the strongest here, and, as will be noticed in Appendix II, disappears on diluting the acid.

CADMIUM SULPHATE ($CdSO_4$).

(Saturated, and dilute $\frac{1}{3}$ H_2O solutions. Fig. 85.)

The reflecting power is, of course, much lower for solutions. Curve *b* shows that the reflection band is asymmetrical. The maximum occurs at 9.2 μ. The absorption band at 4.6 μ is harmonic with this one. This reflection band was found by Pfund[1] for the solid crystal at 9.1 μ—more nearly 9.15 μ, as read on the published curve. Water has no reflection bands in this region.

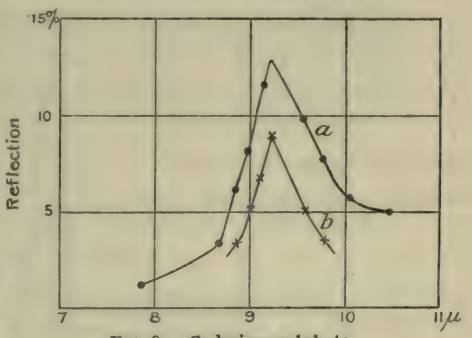

FIG. 85.—Cadmium sulphate.

NICKEL SULPHATE ($NiSO_4+7H_2O$).

In fig. 86 are given the curves (*a*) for a saturated solution of $NiSO_4$, and (*b*) for a solution diluted to about one-half, while curve *c* is for a large, solid crystal which was not highly polished. The curves for the

[1] Pfund: Paper presented at the meeting of the Amer. Phys. Soc., April 20-22, 1906.

saturated solution indicate that the reflection band is complex, with maxima at 9.15 and 9.5 μ, the latter being coincident with that of H_2SO_4. This is better illustrated in the curve for the dilute solution, in which the band at 9.1 μ has quite disappeared.

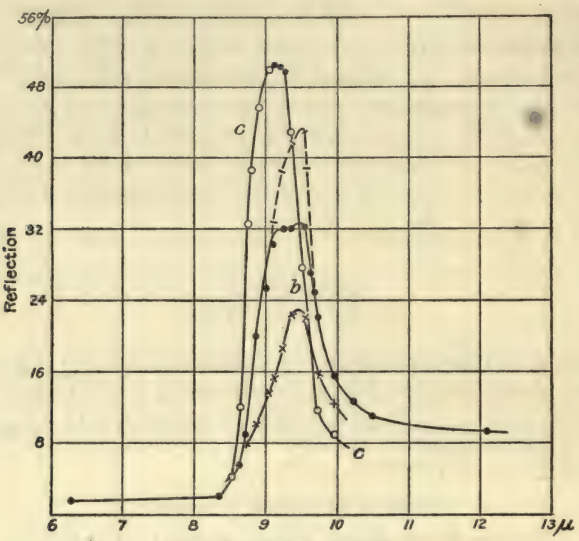

FIG. 86.—Nickel sulphate.

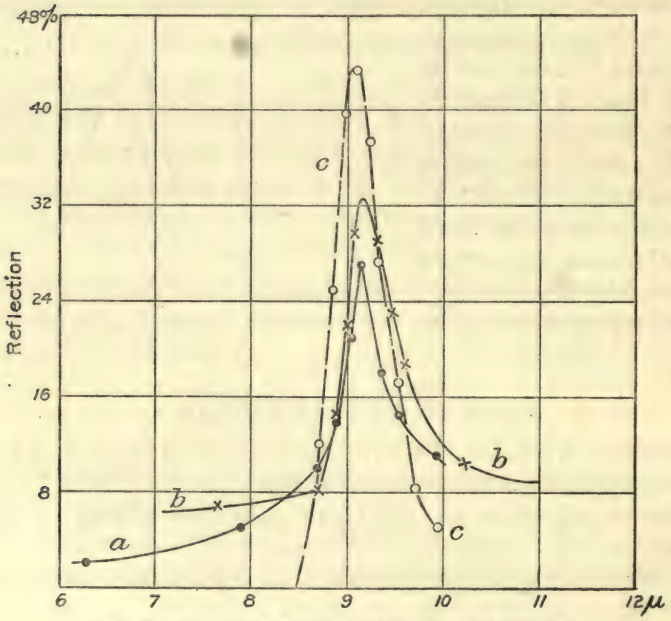

FIG. 87.—Copper sulphate (*a*) and (*c*); Zinc sulphate (*b*).

The reflection band of the solid crystal does not agree with the one found by Pfund at 9.05 μ, which is the mean value of the present curve. In the present curve the maximum is evidently complex. Neither does the maximum of the solid and that of the solution agree, which is probably to be expected. In fact, the study of solutions was undertaken to test this very point.

Copper Sulphate ($CuSO_4+5H_2O$).

In fig. 87, curve *a* is for a saturated solution of copper sulphate in which the maximum of reflection is very sharp at 9.15 μ. For a solid crystal of this material the maximum (curve *c*) coincides with that of the solution. The reflection band found by Porter at 2.3 μ really occurs at 3.3 μ. The former value is due to an error in computation.

Zinc Sulphate ($ZnSO_4+7H_2O$).

The reflecting power is somewhat higher than in the preceding compound. The maximum (curve *b*, fig. 87) occurs at 9.2 μ for a saturated solution of this compound.

Sodium Sulphate ($NaSO_4+10H_4O$).

The selective reflection of a saturated solution of this compound is shown in curve *a*, fig. 88. The maximum occurs at 9.2 μ, while Pfund found it at 9.02 μ, using the surface of a mass of crystals.

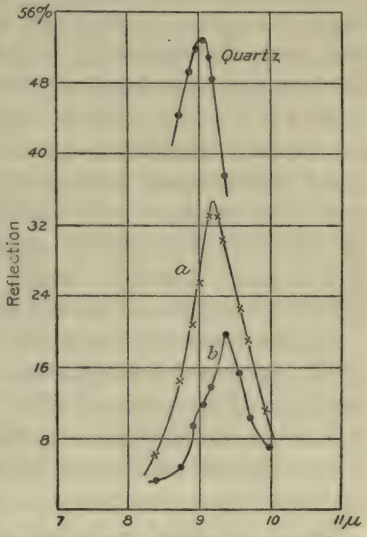

Fig. 88.—Sodium sulphate (*a*); Potassium sulphate.

Mercury (Hg).

Several observations were made on the reflecting power of mercury, but the present arrangement was not well adapted to determine the absolute reflecting power, and no thorough examination was made. The chief difficulty is in having the two surfaces at the same level. Values of reflecting power as high as 85 per cent (purity not known) were observed, while the computed value is 90 per cent at 12 μ.

Earth tremors had but little effect on the surface; while, if pure dust-free mercury be used, this is the best substance available to compare the effect of the polish upon the reflecting power in the region of short wave-lengths. In fact, the determination of the absolute reflecting power throughout the spectrum would be an interesting study by itself.

Potassium Sulphate (K_2SO_4).

Curve *b*, fig. 88, is for a saturated solution of this compound. There appear to be two maxima—a small one at 9.1 μ, and a much larger one at 9.4 μ—which disagrees with Pfund, who found a maximum at 8.85 for the reflection from the plane surface of a mass of these crystals.

The results, as a whole, show that the single narrow reflection bands of several of the sulphates at 9 μ is complex, and is shifted toward the long wave-lengths when dissolved in water, while in others this band remains single, and is not shifted in solution. The reflection of most of the solids was found by Pfund (loc. cit.). In some cases we agree in the location of the maxima, while in other cases (solids *vs.* solutions) we do not agree. This is not, in any inherent errors, in adjustment of the present instrument, for at the conclusion of the work the quartz band at 9.05 μ was found at its proper place, as shown in fig. 86. Neither is it due to errors in Pfund's apparatus (although his dispersion was not so great), for we agree in the position of the maxima of quartz, glass, Iceland spar, potassium nitrate, copper sulphate, and sulphuric acid. The solutions were examined on the same day and in the following order: H_2SO_4 and the sulphates of Cd, Ni, Cu, Zn, K, Na. The disagreement is in Ni, Zn, K, Na, which means that the instrument could not have gotten out of adjustment during the examination.

The conclusion to be drawn is that several of these sulphates, viz, Ni, K, Na, and possibly Cd, are dissociated, or that the intra-molecular condition of the molecule (the "bonding") has become similar to that of H_2SO_4. Possibly hydrates have been formed. But what may we say of the sulphates of Ba, Sr, and Mg, which in their solid (anhydrous) condition have several bands, some of which lie close to those of H_2SO_4?

The more logical way of attacking this problem would have been to examine[1] the solid crystals at the same time as the solutions; but life is too short for one man to do all this, and the aforesaid line of reasoning excludes the possibility of the disagreement being due to instrumental errors, which would have to amount to from 4 to 6 min. of arc to account for the shifting of some of the maxima. In Cu and Cd the shift, if any, is very slight, although the Cd band is evidently complex.

In the sulphates of Ni, K, and Na a definite shift has been noted, and is similar to the effect observed in solutions of iodine in CS_2, and in C_2H_5OH in the visible spectrum. No doubt a solvent may exist, in which the 9.1 μ band of $CuSO_4$ is also complex.

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[1] Since writing this the author has examined the sulphates of Ni and Cu in the solid state and in solution. The maximum of solid $CuSO_4$ and of the solution in water occurs at 9.12 μ, while in $NiSO_4$ the complex band of the solid at 8.9 to 9.15 μ is shifted to 9.2 to 9.5 μ in solution.

SUMMARY.

The transmission and reflection spectra of at least 125 elements and compounds have been examined, many of them to 15 μ, by means of a mirror spectrometer, a rock-salt prism, and a Nichols radiometer. The aim of the investigation was the study of a series of minerals containing oxygen and hydrogen in the form of what is known as water of constitution and water of crystallization. The interpretation of the results are based upon the assumption that if the union of the oxygen and the hydrogen in the molecules is similar to that of water, then the absorption spectra of minerals, containing these two elements thus united. should show the absorption bands of water superposed upon the absorption spectrum of the other constituents.

On the other hand, minerals containing oxygen and hydrogen as water of constitution should not show the water bands, except hydroxyls, which should show a band at 3 μ.

The results show that of some 30 minerals containing "water of crystallization" there are no important exceptions to the rule that they should show the bands of water. On the other hand, the one important exception to the rule that minerals containing "water of constitution" should *not* show water bands is cane sugar. Minerals containing hydroxyl groups generally have a marked band at 3 μ. Sulphates have a strong band at 4.55 μ, and a less constantly recurring band at 9.1 μ, due to the SO_4 ion. On the other hand, the silicates do not have such definite bands, which would seem to indicate that the union of the silicate radical is different in each mineral containing that element. In Table III are given a list of groups of atoms which have characteristic absorption bands.

TABLE III.

Compounds having the following groups.	Show characteristic absorption bands at :		
CH_2 or CH_3	3.43	6.86	13.6–13.8 and 14 μ
NH_2	2.96	6.1 to 6 15 μ	
C_6H_6	3.25 μ	6.75 8.68 9.8 11.8 12.95 μ	
NO_2		7.47 9.08?	
OH		3.0 μ	
NCS		4.78 μ	
SO_4	4.55	8.7	9.1 μ

The examination includes minerals of which the chemical constitution is in doubt; for example, talc and serpentine. The former is not supposed to contain hydroxyl groups, while in the latter such groups are inferred. The present research supports these views in that the transmission curve of talc does not contain an absorption band at 3 μ;

while serpentine contains a large band at 3 μ, which is in common with substances containing hydroxyl groups.

The reflecting power of the metals Zn, Co, Al, Cd, Pd, and Ir is high, and the observed values at 12 μ are in close agreement with those computed from their electrical conductivity. It is a remarkable fact that the region of the first occurrence of selective reflection of the majority of substances examined (other than silicates) lies between the wavelengths 8 to 10 μ. This is probably to be expected. Drude[1] has shown that the infra-red free vibrations (Eigenschwingungen) depend upon the ponderable mass of the molecule, and, from this, that one can obtain some idea of the molecular weight of the substance.

The study of the reflecting power of solids in solution is not sufficiently extended to draw general conclusions, but the data shows that the method is feasible—that the reflecting power is proportional to the concentration—and that the maxima may or may not agree with those of the substance in the solid state, depending probably upon the solvent, just as is true of the visible spectrum. A notable example is iodine, in CS_2 and in C_2H_5OH. The experiment also shows that a single band of a mineral in a solid state may appear as several bands when in solution. This is an interesting field that deserves further investigation. The difficulties involved are not greater than for absorption spectra, while the intensity of the energy is still quite large in this region of the spectrum. In the visible spectrum it is known that different maxima appear, depending upon the solvent and upon the addition of acids to the solvent. But the visible spectrum is so narrow in comparison with the absorption bands that the infra-red is far better adapted to the study of this phase of the problem.

As mentioned in the text, the chief difficulty in this research was in obtaining minerals suitable to illustrate the questions involved. This has placed the writer under deep obligations to the late Prof. S. L. Penfield, of Yale University, who donated a number of rare minerals not obtainable from dealers, and to the officials of the U. S. National Museum, who also supplied a large number of specimens. The Director of the Bureau of Standards generously supplied apparatus and material. I am also under obligations to Dr. J. C. Blake, whose advice on the mineralogical side of this question was frequently sought.

WASHINGTON, D. C., *June 20, 1906.*

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[1] Drude: "Optische Eigenschaften und Elektronentheorie," Ann. d. Phys., 14, pp. 677 and 936, 1904.

TABLES OF MAXIMA.

TABLE V.—MAXIMA OF INFRA-RED ABSORPTION AND REFLECTION BANDS.

Anhydrite. $CaSO_4$.	Selenite. $CaSO_4+2H_2O$.	Quartz. SiO_2.	Opal. SiO_2+xH_2O.	Heulandite. $H_4CaAl_2Si_6O_{18}+3H_2O$.	Stilbite. $CaAl_2Si_6O_{16}+6H_2O$.	Potassium alum. $K_2SO_4Al_2SO_4+24H_2O$.	Natrolite. $Na_2Al_2Si_3O_{10}+2H_2O$.	Scolecite. $CaAl_2Si_3O_{10}+3H_2O$.	Analcite. $Na_2Al_2Si_4O_{12}+2H_2O$.	Colemanite. $Ca_2B_6O_{11}+5H_2O$.	Calcium chloride. $CaCl_2+6H_2O$.	Potassium ferrocyanide. $K_4Fe(CN)_6+3H_2O$.	Apophyllite. $H_7KCa_4(SiO_3)_8+4\frac{1}{2}H_2O$.	Deweylite. $H_4Mg_4(SiO_4)_3+4H_2O$.	Thomsenolite. $NaCaAlF_6+H_2O$.
1.9 μ	1.5	2.9	1.46	1.48	1.47	1.5	1.5	1.5	1.5	1.5	1.48	1.48	1.5	3.0	1.4
3.2	2.05	4.37	1.98	2.0	1.95	2.0	2.0	2.0	2.0	2 0	2.04	2.0	2.0	5.7	2.0
4.55	3.0	5.0	3.0	3.0	3.0	R.	3.1	3.1	2.96	2 95	3.15	3 0	3.0	6 05	2.7
5 7	4 65	5.3	4.23	4 4	4.7	9.1	4.62	4.4	4.8	R.	4.75	4.12	R.	R.	3.0
6.15	R.	5.9	5	4.75	6.05		6.1		6.15	7.3	6.3	5.0	9.15	9.6	4.65
6.55	8.7	6.22	5.3				7.4			9.4		6.2	9.7	10.5	
Refl.		6.65	6.1				R.			10 6					
8.6		R.	6.6				9.03			11.05					
9.05?		8.49					9.5								
		9.03					10.08								
		12.5													

Gismondite. $H_4(Na_2Ca)Al_2Si_6O_{18}+4H_2O$.	Blödite. $MgSO_4Na_2SO_4+4H_2O$.	Thaumasite. $CaSiO_3CaCO_3CaSO_4+15H_2O$.	Hydrotalcite. $Mg_3Al(OH)_8$.	Varicite. $AlPO_4+2H_2O$.	Vivianite. $Fe_3P_2O_8+8H_2O$.	Mellite. $Al_2C_{12}O_{12}+18H_2O$.	Cassiterite. SnO_2.	*d*-Fructose. $C_6H_{12}O_6$.	Dextrose. $C_6H_{12}O_6+H_2O$.	Cane sugar. $C_{12}H_{22}O_{11}$.	Maltose. $C_{12}H_{22}O_{11}+H_2O$.	Lactose. $C_{12}H_{22}O_{11}+H_2O$.	Raffinose. $C_{18}H_{32}O_{16}+5H_2O$.	Gum arabic. $2C_6H_{10}O_5+H_2O$.	Rochelle salt. $NaKC_4H_4O_6+4H_2O$.
1.4	1.5	1.5	1.5	1.5	1.48	1.4	3	3.25	1.5	1.5	1.5	1.5	1.5	1.48	1.5
2.0	2.0	2.05	2	1 9	2.05	2.0	5.8	5.8	3.0	3.0	2.15	3 to	2.0	2.0	2.1
3.0	3 to	3.0	3 to	3 to			6.6		to	3.4	2.6	3.7	3.0	3.0	3 to 4
4.75	3.5		3.8	3 8			7.3		3.8	4.75	3 0	4.75	3 3	3.4	4.75
	4.7		4.75	4.75			8.25		4.75	6.0	3.4	6.1	4.75	4.75	
	5.6		R.	6 4			9.7		6.0		4.75		6.03		
	6.0		9.9	R.			10.5				6.2		7.1		
				9.25									7 4		
				9.72									8.1		
													9 to		
													10.5		

TABLE V.—MAXIMA OF INFRA-RED ABSORPTION AND REFLECTION BANDS—Continued.

Brucine. $C_{23}H_{26}N_2O_4+4H_2O$.	Manganite. $MnO(OH)$.	Göthite. $FeO(OH)$.	Bauxite. $Al_2O(OH)_4$.	Turquoise. $AlPO_4Al(OH)_8+3H_2O$.	Lazulite. $Mg,Fe,Al_2(OH)_2(PO_4)_2$.	Hydrargillite. $Al(OH)_3$.	Diaspore. $AlO(OH)$.	Datolite. $Ca(BOH)SiO_4$.	Brucite. $Mg(OH)_2$.	Portland cement.	Mannite. $C_6H_8(OH)_6$.	Chloral hydrate. $CCl_3CH(OH)_2$.	Prehnite. $H_2Ca_2Al_2(SiO_4)_3$.	Hydronephelite. $HNa_2Al_2(SiO_4)_3+3H_2O$.	Pectolite. $HNaCa_2(SiO_3)_3$.
1.5	3.2	3.1	2.9	3.3	3.0	3.0	1.9	2.2	2.5	3.0	1.6	1.5	2.9	2.8	2.5
1.95	6.2	5 7	to	5.1	4.3	5.2	3.0	2.8	2.7		2.1	2.0		4.1	3.4
2.4		9.1	3.6	5.35			5.0	4.8	3.0		3.4	3.0		5.0	3.95
3.4			4 75	5.65			6.7	5.3	5.0		3 8	3.2		5.95	4.55
4.75			5.8	6.3			R.	6.2	6.7		5.0	3.8		6.8	R.
5.1			7.0	7.6			8.56	R.	7.7		6.1	4.6		7.3	9.4
6.0							9.45?	8.8	8.2			5.1			10.3
6.8							9.8	9.2				5.7			10.8
7.2							10.2	9.5				6.2			
7.85							12.8	10.01				7.1			
8.3							13.85	10.8				8.0			
9.0							14.6	11.2							
9.2															
9.7															
10.0															
10.8															
11.3															
11.6															
11.9															
12.3															
12.7															
13.3															

Chloritoid. $H_2(Mg,Fe)Al_2SiO_7$.	Clinochlore. $2H_8Mg_5Al_2Si_3O_{18}$.	Muscovite mica. $H_2KAl_3(SiO_4)_3$.	Biotite mica. $(1\frac{1}{2}K)_2(Mg,Fe)_3Al_2Si_3O_{12}$.	Serpentine. $H_4(Mg,Fe)_3SiO_9$.	Talc. $H_2Mg_3Si_4O_{12}$.	Epidote. $HCa(AlFe)_3Si_3O_{13}$.	Barite. $BaSO_4$.	Glauberite. $Na_2SO_4CaSO_4$.	Thenardite. Na_2SO_4.	Kieserite. $MgSO_4+2H_2O$.	Celestite. $SrSO_4$.	Anglesite. $PbSO_4$.	Cadmium sulphate. $3CdSO_4+8H_2O$.	Sulphuric acid. H_2SO_4.
2.2	2 9	2.85	2.8	3.0	5.58	1.6	3.2	2.35	3.1	1.45	3.2	1.9	1.5	3.6
3.2	4.9	3.5	5.0	4.2	5.95	2.1	4.6	4.55	4.55	1.83	4.55	3.2	2.05	R.
5.6	5.9	5.6	5.6	5.0	7.25	3.0	6.2	5.65		3.0	6.4	4.5	3 to	7.2
6.3	6 28	5.95	5.95	6.6	R.	4.3	6.5	6.2		4.55	R.	4.97	3.4	8.6
	7.1	6 3	6.2	7.3	9.03	5 0	R.	R.		6.05	8.2	6.4	4.6	9.55
	7.18	7.1	6.6	8.1	9.74	5.3	8.34	8.3		R.	8.76	6.75	R.	10.4
		R.	7.2	8.5		5.65	8.9	8.7		8.7	9.05		9.2	11.35
		9.2	R.	R.		5.95	9.1	9.05		9.25				
		9.7	9.3	9.7		6.7								
			9.6	10.5		7.4								
			9 85											

TABLE V.—MAXIMA OF INFRA-RED ABSORPTION AND REFLECTION BANDS—Continued.

Potassium dichromate. $K_2C_2O_7$.	Potassium chlorate. $KClO_3$.	Apatite. $Ca_5F(PO_4)_3$.	Garnet. $Ca_3(Fe,Mg)_3Al_2(SiO_4)_3$.	Monazite. $(Ce,La,Di)PO_4$.	Willemite. Zn_2SiO_4.	Collodium. $C_6H_7O_2(ONO_2)_3$.	Ammonium chloride. NH_4Cl.	Sodium biborate. $Na_2Br_4O_7$.	Silver. $AgNO_3$.	Sphalerite. ZnS.	Orthoclase. $KAlSi_3O_8$.	Amphibole. $CaMg_3(SiO_3)_4$.	Zircon. $ZrSiO_4$.	Albite. $NaAlSi_3O_8$.
2.9	3.2	2.9	1.2	From	2.9	1.6	1.62	1.9	2.7	1.5	2.75	2.85	2.15	2.85
3.2	3.6	4.8	to	3.2	5.9	2.8	2.2	3.0	3.6	2.7	4.7	4.8	3.1	5.7
3.7	5.24	5.9	2.8	to 5.3	6.9	3.5	2.95	3.7	4.12	to	5.3	6.0	3.6	6.3
5.4	6.27	6.5	4.3		R.	6.05		4.75	4.78	3.2	5.7	6.8		R.
5.9	6.93	6.9	to 4.		10.1	7.3		R.	5.66	11.2	6.3	7.4		8.7
6.65		R.			10.6	7.85		7.5	R.	13.2	R.	R.		9.7
7.7		9.1			10 98	8.7		9.6	7.45		8.8	8.7		10.0
8.7		9.7				9.1		to 10			9.8	9.45		10.5
						9.5						10.02		
						10.0								
						10.8								
						11.7								
						12.15								
						12.7								
						13 6								

Enstatite. $MgSiO_3$.	Ebonite.	Potassium nitrate. KNO_3.	Calcite. $CaCO_3$.	Ferrous sulphate. $FeSO_4+7H_2O$.	Magnesite. $MgCO_3$.	Microcline. $KAlSi_3O_8$.	Sodium meta phosphate. $NaPO_3$.	Tourmaline. $H_6Na_2Fe_4Al_8Si_{12}O_{62}$.	Granite quartz. Mica feldspar.	Nickel sulphate. $NiSO_4+7H_2O$.	Copper sulphate. $CuSO_4+5H_2O$.	Zinc sulphate. $ZnSO_4+7H_2O$.	Sodium sulphate. $Na_2SO_4+10H_2O$.	Potassium sulphate. K_2SO_4.
1.82	3.4	3.5	3.45	R.	3.2	R.	3.9	1.25	R.	Solid	Solid.	Solid.	Solid.	Solid.
2.9	5.9	4.0	3.93	9.1	3.8	8 84	5.5	2.75	8.5	R.	R.	R.	R.	R.
5.0	6.9	4.65	4.65		4.6	9.5	6.0	R.	8.8	8.9?	9.1	9.2	9.2	8.85
R.	8.25	5.6	5.7		R.	9.92	R.	7.45	9.22	9.15	Solu-		Solu-	Solu-
9.12	9.1	7.15	6.7		6.5		8.0	8.0	9.6	Solu-	tion.		tion.	tion.
	9.9	9.6	6.9		6.8		9.4	9.25	9.9	tion.	9.12		9 2	9.05
		10.2	8.5					9.7	10.7	9.2				9.4
		12.0	9 4					10.8		9.5				
		13.0	10.0											
		14.3	10.7											
			11.3											
			12.2											
			12.5											
			13.2											

APPENDIX I.

THE TEMPERATURE OF THE MOON.

I.

From his Mount Whitney observations[1] Langley concluded that the soil of an airless planet at the moon's distance from the sun would have a temperature not greatly above —225° C. His later observations on the radiation (reflection) from the moon led him to conclude that the temperature of the sunward surface of the moon is about 0° C. This inference, he mentions, is contradictory to the one drawn from the Mount Whitney observations, which in themselves he considered exact. "The most reliable spectrum comparisons with a blackened screen show an average effective temperature of +45° C., near the time of full moon."[1] He could detect *no radiation* from the *dark* moon. For the bright moon, his spectrum radiation curves rise from a zero value at 6 to 7 μ to a maximum at 8.6 μ, with a smaller maximum at 10 μ. There are absorption bands, due to atmospheric water, at 6 μ and 9.6 μ.

He found also *direct radiation from the sun* in this region, but does not consider it in arguing for a direct radiation from the moon. He considered that the part of radiation from the moon, which was transmitted by glass, is reflected energy from the sun, whereas the part absorbed by glass is radiation from the moon. The same assumption was also made by Lord Rosse, but it is untenable if we admit a selective reflection of the moon. To the writer the line of reasoning seems false, in the light of our present knowledge of infra-red radiation, and a better criterion for judging whether or not the surface of the moon becomes appreciably warmer under the rays of the sun would seem to be to reëxamine the rapidity of the fall and rise in intensity of the radiation from the moon during an eclipse. Langley (loc. cit.) made observations on the eclipse of September 23, 1885, which indicate a sudden and very rapid falling off in the heat as the eclipse commenced, with some indications of a rise nearly as rapid after its conclusion. In fig. 89 are plotted his observed galvanometer deflections during the progress of the eclipse. The ordinates are galvanometer deflections; the abscissæ are the predicted times in hours to mid-eclipse. The three curves are for the center, the east, and the west limbs of the moon. The observations were interrupted by the rapid formation of clouds just at the predicted time for the moon to leave the umbra. The eye observations showed

[1] Mem. Nat. Acad. Sci., 4, p. 197, 1887.

an anomalous distribution of light, which was thought to be due to variations in the terrestrial atmosphere at different points along the great circle at which the solar rays touched the surface. However, the results as a whole show a sudden change in the radiation (reflection) from the moon, with change in illumination. The penumbra began to affect the center of the moon at $+1^h\ 44^m$. The predicted time for the moon to enter the penumbra was $+2^h\ 48^m$. In other words, in the short time of about 1.5 hours, in passing from the penumbra into the umbra, the radiation from the west limb has fallen from a maximum to a minimum value. Without actually computing[1] this fall in radiation, which is so sudden as to indicate a small conductivity and a very superficial cooling, one would think that at the beginning of totality the radiation would still be detectable.

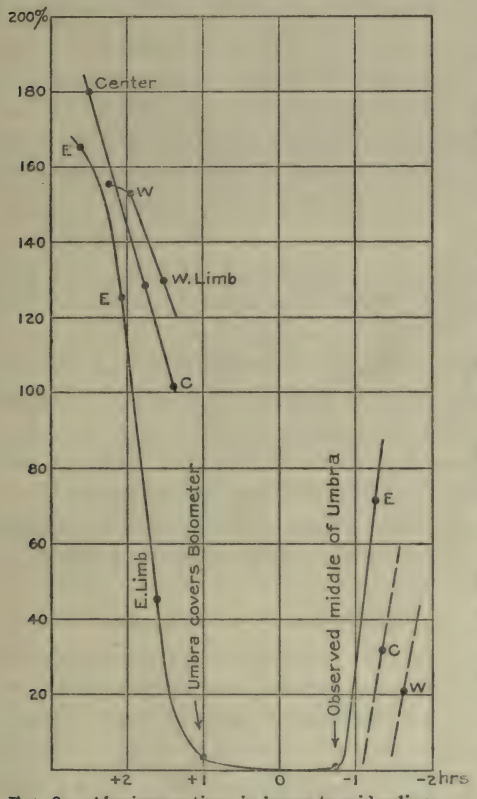

FIG. 89.—Abscissas = time in hours to mid-eclipse; ordinates = galvanometer deflections.

The question of the gain (or loss) of heat on the surface of an isolated body like the moon does not lend itself readily to a coherent line of reasoning, because of the fact that we know so little about the phenomena connected with it. A thin surface, like a radiometer vane, placed in a vacuum and subjected to radiation, acquires a maximum temperature in a very short time. The same is not true of the earth and its atmosphere, isolated in space. It is difficult to say what one ought to expect of the moon, but from ordinary experiences one would anticipate an appreciable lapse of time for the surface to acquire an extreme change in temperature, after subjecting it to the sun's heat.

At great elevations on the earth, where the atmosphere is rare, we know that the soil grows colder, although the direct rays become hotter with rise in height, and one would infer that similar conditions obtain over the whole lunar surface.

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[1] See page 115.

Harrison[1] inferred that the surplus heat of the moon will reach its maximum several days after the day of complete illumination. In commenting on this statement Langley (loc. cit.) reminds the reader that the region of the moon, which has received at first quarter the solar rays for rather more than four days, after being subjected to the most intense cold during the moon's long night, has been but very little warmed in comparison with the surface illuminated at last quarter, which has been heated during a mean duration of eleven days, so that at the last quarter the heat of the moon is certainly not less than at the full.

During the eclipse of October 4, 1884, Boeddicker[2] showed that the moon parts with its acquired heat very rapidly, and "it is hard to admit that this heat from the lunar surface, which the moon has been absorbing during many days of continuous sunshine, is parted with at once, the whole earthward surface of the planet cooling almost instantaneously."[3]

From alternate exposures on bright and dark spots Langley found that the radiation from the bright region around Tycho exceeded that from the dark surface of the Mare Imbrium by 31 per cent, and as a whole found that the bright parts of the moon radiate about 14 per cent more than the dark parts. This is evidently due to a larger reflection of sunlight. "If the same holds good for the invisible solar rays, it is certain that less of the sun's heat is absorbed by the bright parts, and hence there is a possibility that the temperature and proper radiation of the light regions are less than those of dark areas, though this would not necessarily follow, since many other factors must be included."[3]

II.

The writer has examined the infra-red reflecting power of a series of minerals, including quartz, feldspars, amphiboles, and micas, which are the chief constituents of the rocks of the earth's crust, and has found a uniformly decreasing reflecting power of 3 to 5 per cent at 4 μ to 0.3 per cent at 7 μ, followed by bands of selective reflection from 8.5 to 10 μ. In this latter region the mean reflecting power is from 40 to 50 per cent for silicates, while pure quartz has a reflecting power of 90 per cent. The reflection curves are given in fig. 90 in a condensed form. In the lower part of the figure several of Langley's lunar radiation (reflection) curves are given, in which the ordinates are in arbitrary units. Of course, the absolute reflecting power of the moon is unknown. Zöllner has shown that, owing to the irregularities of its surface, the full moon

[1] Harrison: British Assoc. Report, 1866, II, p. 20.
[2] Boeddicker: Nature, 30, p. 589, 1884.
[3] Langley: Mem. Nat. Acad. Sci., 3, p. 17, 1884.

does not reflect as a smooth sphere would do, but very nearly as a flat disk of like reflecting power and filling the same angle. Such a disk, if it diffused all the solar energy which falls on it, would send to us $\frac{1}{97800}$ of what the sun does, provided it reflected perfectly in all directions the total incident solar energy. The moon, however, is not such a reflector, and in the visible spectrum the solar light is about 500,000 times moonlight. On this scale the curves of the moon given in fig. 90 would not be visible. The depression in the lunar curves at 9.6 μ is

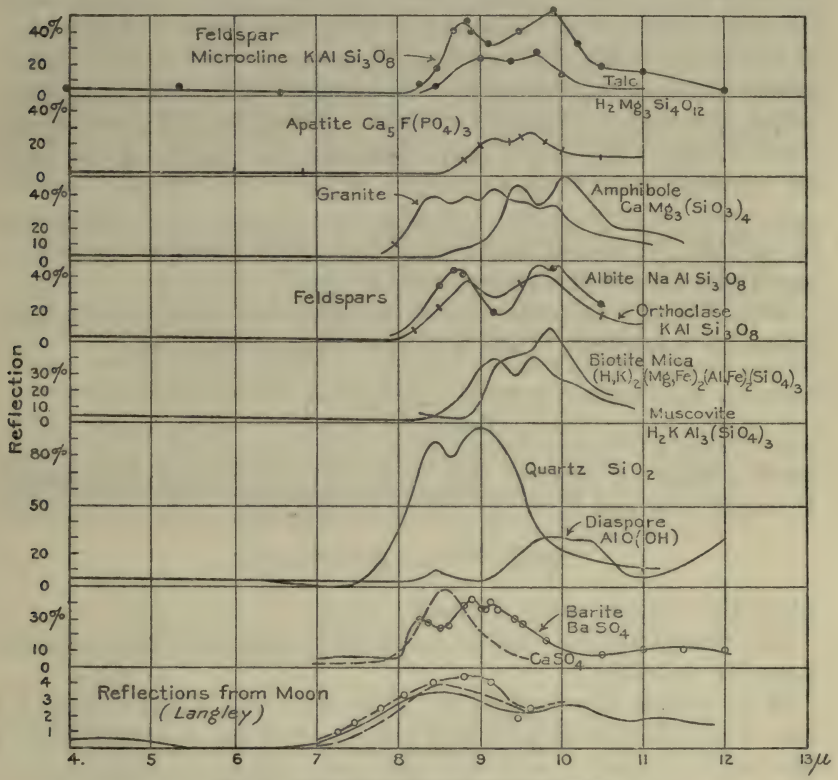

FIG. 90.—Reflection curves of various silicates.

due to an atmospheric water band. The region from 5 to 7 μ likewise contains water bands. One can readily see from these curves that a reflecting surface composed of rocks like granite, basalt, diorite, etc., which are mixtures of feldspar, hornblende, and mica, would give a curve similar to that of the moon.

The general assumption is that the crust of the earth and of the moon have the same constitution, viz, a series of silicates. It follows from the present research that the earth and the moon may be considered

selectively reflecting surfaces, with a band of metallic reflection from 8.5 to 10 μ. Hence, in the region of the spectrum from 4 to 7 μ only 3 to 5 per cent of the radiation from the sun will be reflected from the moon, under the best surface conditions, while in the region from 8 to 10 μ the reflecting power will rise to 50, or even 90 per cent. Under the worst conditions the balance will still be in favor of the region of 8 to 10 μ.

The occurrence of the maxima of the reflection curves and Langley's observed emission curve of the moon (that part which is transmitted in the transparent region of the earth's atmosphere between 7 and 10 μ) in this region of the spectrum may, of course, be nothing more than a mere coincidence, and the author calls attention to it merely as an interesting side issue to the main research. The reflecting power of the moon for visible rays is only $\frac{1}{500000}$ full sunlight. Assuming that at 9 μ the reflecting power is, on an average, 20 times this, the value becomes $\frac{1}{25000}$, or 0.00004 per cent. Assuming the temperature[1] of the moon to be 300° abs., we can get some idea of its emissive power at 9 μ, as compared with the sun at a temperature[2] of 5500°.

From Planck's formula[3] for the distribution of energy in the spectrum of a "black body" (which, of course, the moon is not)

$$I = c_1 \lambda^{-5} \left(e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1}$$

we can obtain a ratio of the intensities for the two temperatures $T_1 = 300°$ abs. and $T_2 = 5500°$ from the formula

$$(E^{c_2 \div \lambda T_2} - 1 \div E^{c_2 \div \lambda T} - 1)$$

where $C_2 = 14{,}500$, using λ (max.) $= 9$ μ.

This ratio is 0.0016. But the moon, not being a black body, will have a smaller emissivity.

If its surface were of iron oxide[4] its emissivity would be only 0.3 that of a black body at 300°, and, judging from the rapid decadence of the radiation curve (which may indicate a low conducting material) during an eclipse (fig. 89), its emissive power may be even less than

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[1] Very: Astrophys. Jour., 8, 199, 1898; also Langley, loc. cit.; Poynting: Jahrb. der Radivaktivität und Elektronik, 2, 42, 1905.

[2] Warburg: Verh. Deutsch. Phys. Ges., 1, 2, p. 50, 1899; Day and Van Ostrand: Astrophys. Jour., 19, p. 1, 1904.

[3] Planck: Vehr. d. Deutsch. Phys. Ges., 2, p. 202, 1900; Ber. d. k. Akad. d. Wiss., Berlin, p. 544, 1901.

[4] Kayser: Spectroscopy, vol. II, p. 80.

this, say 0.1. The ratio of the emissive power of the moon to that of the sun will then be 0.00016, which is four times (0.00016÷0.00004) the reflected energy of the sun from the moon. On this assumption, the moon at 0° C. would radiate twice as much as it would reflect from the sun.

This shows that unless there is something radically wrong in the assumptions made, the above coincidence is fortuitous. This, however, does not settle the question, for Langley observed also direct radiation from the sun in this region, and from existing data of the radiation from the moon we do not know how much of it is selectively reflected energy from the sun. Computations which require all sorts of assumptions will not settle the question; but a bolometric comparison of the spectrum energy curves of the sun and of the moon, made at high altitudes, will be of the greatest service in clearing up this matter.

Since writing this appendix I have computed the fall of temperature of the lunar surface, neglecting the conductivity from the interior (which simplified the computation) and find that for an emissivity of 0.3 of a "black body" (iron oxide) the temperature would fall from 300° to 273° abs. in 1.2 hours, while for an emissivity of 0.1, the time would be over 3 hours. By allowing for conductivity these periods would be considerably increased, so that unless the moon's emissivity is considerably higher, the cooling curve will not be coincident with the eclipse curve in fig. 89. Assuming that the sky does not radiate to the bolometer, then the latter would give zero, and finally negative deflections as the temperature falls. Langley does not mention negative deflections from the moon. He records negative deflections for his sky-screen curves.

APPENDIX II.

ADDITIONAL DATA.

As this work goes to press the experiments on selective reflection by Pfund[1] has appeared, and since it contains considerable new data it is added for the sake of completeness. In fact, sulphuric acid was not thoroughly examined by the writer when he learned that another was working in the same field, although the examination of the sulphates demanded it. The sulphates given in the appended table furnish additional evidence of the presence of bands due to the SO_4 ion. Furthermore, the nitrates have a band at 7.45 μ which the writer found in several nitro derivatives[2] of benzine. He was uncertain, however, whether it was caused by the NO_2 group or "ion." In the same manner, the 7.4 μ and 9 μ reflection bands of nitroso dimethyl aniline coincide with the bands found by transmission at 7.4 and 8.9 μ. The transmission curve is very low, and probably most of the bands observed are really due to selective reflection. Again, glycerin has a reflection band at 9.7 μ, which is one of the characteristic bands of the alcohols as found by transmission. No doubt the large absorption bands found by the writer in ethyl succinate from 7 to 8 μ, in cyanine at 6.6 and 13.2 μ, and in methyl salicylate at 7 to 9 μ, are really due to selective reflection, but this material was not at hand when the present reflection work was done. In fact, it is what one would expect to find for such large bands, although there are no data to indicate the necessary size of the extinction coefficient to cause selective reflection. His interesting experiments showing that a substance in a liquid and in a solid state has the same absorption (reflection) maxima is further proof of what the writer found for the absorption bands of several carbohydrates, such as thymol, paraffin, stearic acid, phenol, and menthol at 3 μ, and is, of course, to be expected so long as the "physical molecule" is unchanged, as announced long ago by Stenger. Of more importance are his experiments with sulphuric acid, in which several bands disappear on dilution, which may help clear up a similar case observed by Krüss in the visible spectrum. His reflection curves for fuming sulphuric acid show maxima at 7.25, 8.6, and 10.35 μ, while the writer found absorption maxima at 7.4, 8.7, and 10.37 μ for sulphur dioxide (SO_2). This is an extraordinary coincidence which, it is true, is apparently not very close for the first

[1] Pfund: Astrophys. Jour., 24, p. 19, 1906.

[2] Investigations of Infra-Red Spectra, vol. 1, p. 86.

two maxima. But, when one considers that the bands are wide and completely opaque as found by transmission, while they are very weak as found by reflection (maxima only 7 and 12 per cent), and that they were made by different observers with different instruments, it is not straining matters to consider them to be due to the same ion. For KNO_3, Pfund found the maximum at 7.05 μ (on the published curve it appears to be 7.1 μ), while the writer found the same band at 7.14 μ, so that the discrepancy noted above is more likely to be due to a difference in our calibration curves. Then, too, the maxima found by reflection and by transmission should differ with the latter lying toward the shorter wave-lengths. Whether a gas can have selective reflection will depend mostly upon its extinction coefficient. To examine its reflecting power in its liquid state will be almost impossible because of the dense vapor above its surface.

TABLE IV.

	Reflection maxima.		
NaK tartrate, $KNaC_4H_4O_6+4H_2O$	6.35 μ	7.35 μ	9.05 μ
Magnesium nitrate, $Mg(NO_3)_2+6H_2O$	7.45		
Cobalt nitrate, $Co(NO_3)_2+6H_2O$	7.45		
Ammonium nitrate, NH_4NO_3	7.45		
Calcium nitrate, $Ca(NO_3)_2+4H_2O$	7.45		
Silver nitrate, $AgNO_3$	7.45		
Potassium nitrate, KNO_3	7.05		
Nickel sulphate, $NiSO_4+7H_2O$	9.05		
Cobalt sulphate, $CoSO_4+7H_2O$	9.05		
Copper sulphate, $CuSO_4+5H_2O$	9.15		
Cadmium sulphate, $CdSO_4+4H_2O$	9.10		
Ferric sulphate, $Fe_2(So_4)_3+9H_2O$	9.05		
Sodium, $Na_2SO_4+10H_2O$	9.02		
Potassium, K_2SO_4	8.85		
Fuming sulphuric acid and water, $H_2SO_4+SO_3$	7.25 8.6	8.6 9.6	10.35 11.35
Nitric acid, HNO_3	7.85	10.55	
Glycerin, $C_3H_8O_3$	4.80	9.70	
Na silicate, Na_2SiO_3	9.95		
Nitrosodimethyl-aniline, $(CH_3)_2NC_6H_4NO$	7.4	9.0	

It is generally conceded that when a gas is dissolved in a liquid, part of the gas goes into solution, part will be actually liquefied, while part may enter into chemical combination with the liquid. Since change of state does not affect the absorption (reflection) bands, it would appear feasible to examine the reflecting power of gases by this method. However, the question of the solubility of gases in different liquids is also a quite unexplored field, so that the investigator would first have to search for proper solvents.

APPENDIX III.

EMISSION SPECTRUM OF BURNING CARBON DISULPHIDE AND CORRECTIONS TO THE WORK OF JULIUS.[1]

It is becoming more and more a recognized fact that the infra-red spectrum is the seat of great disturbances which can be attributed to well-known groups of chemical atoms or "ions." The pioneers in this field of investigation were Ångström and Julius. Their interest in the subject dates back to the time when rock salt first became recognized as a means for producing the heat spectrum. The dispersion of rock salt was then undetermined beyond 5 μ, and in order to express their emission and absorption bands in wave-lengths they adopted a tentative method of extrapolation, which, since then, has been found to be erroneous. In the meantime, data on infra-red spectra have continued to accumulate, which are often in violent disagreement. For example, CS_2 is variously quoted as having an absorption band at 6.7 to 8.4 μ, while the true value is about 6.8 μ.

During the past few years the writer has attempted to determine the values of the maxima of absorption and emission as accurately as possible in absolute value of wave-lengths, and thus bring a little harmony out of this chaos. This means repeating part of the work of others in order to get a check upon the extrapolation. One of the most interesting pieces of work of this type is that of Julius, who found the emission spectrum of gases during combustion. It contains a very considerable amount of careful work, certain parts of which appear to have gone quite unnoticed by later investigators. It is of no little interest, for it contains evidence of emission bands farther in the infra-red than subsequent work, along other lines, has been able to show. These bands belong to the acid elements and appear at low temperatures, *i. e.*, they do not appear in spark (and arc ?) spectra. This is just the opposite of what the writer found for the basic elements (metals) in which no emission bands were found beyond 2 μ. Perhaps this may eventually give us some clue to the mechanism of radiation. We have two sharp distinctions between the acid and the basic elements. The metals have selective absorption in the short wave-lengths, are opaque to infra-red rays, and no emission lines have been found beyond 2 μ. In fact, according to Pflüger's work, the maximum of the emitted energy lies in the short wave-lengths beyond the visible spectrum. On the other hand, the acid elements have selective absorption bands throughout the spectrum and have emission lines extending far into the infra-red, which generally coincide with the marked absorption bands. The question of the

[1] Julius: Licht- und Wärmestrahlung Verbrannter Gase., Berlin, 1890.

coincidence of the emission and absorption bands led the writer to undertake the present work.

A previous examination of the absorption spectra of gases showed very marked bands in SO_2 which were in quite close coincidence with the emission lines of the products of combustion of carbon disulphid, as given by Julius. The absorption spectrum[1] of CS_2 has a very large absorption band at 6.8 μ (opacity from 6.6 to 7.0 μ) and smaller bands

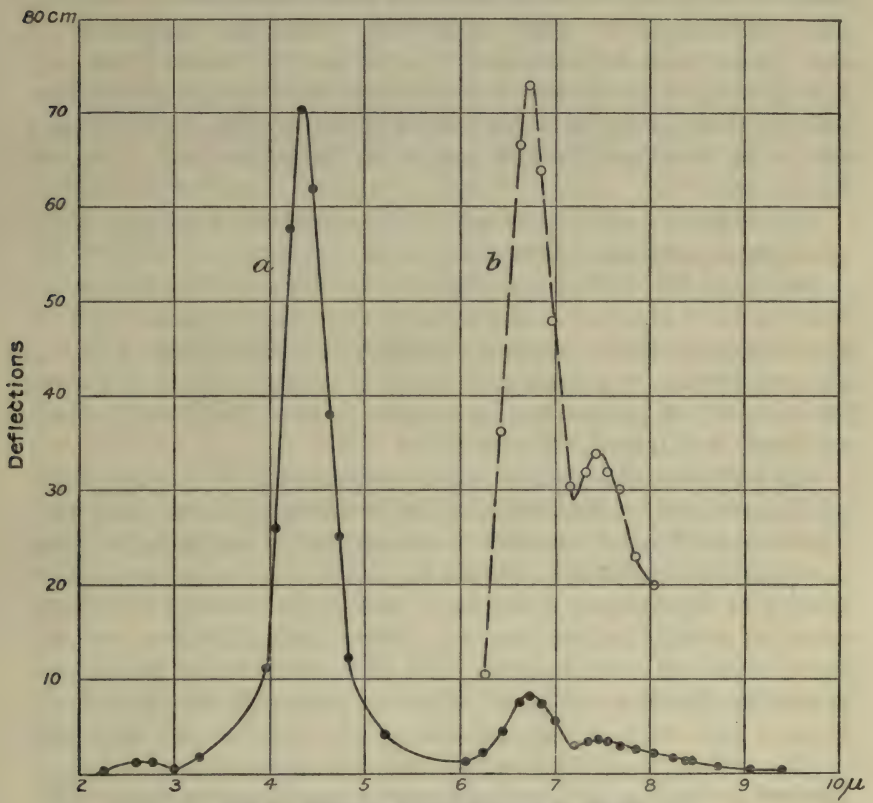

FIG. 91.—Emission of burning carbon disulphide.

at 4.6 and 11.65 μ, while SO_2 has a very large band at 8.7 μ, a somewhat narrower band at 7.4 μ and several small bands; H_2S has a series of small bands which can hardly be considered in the question of the combustion products of CS_2. In fig. 91 is given the emission curve of burning CS_2. In curve *a* the maximum at 4.35 μ is reduced to one-half the scale of the rest of the curve. In curve *b* the bands at 6.75 and 7.45 μ have been magnified 10 times to bring out the sharpness of the maxima. In the

[1] See Investigations of Infra-Red Spectra, vol. I.

present examination the lower part of the flame was examined. The lamp consisted of a tin lubricating-oil can, the neck of which was 5 cm. long, to prevent heating the CS_2 and thus avoid an explosion. Julius (loc. cit.) examined the upper and the central parts of a CS_2 flame and found that for the central region the maximum at 6.75 μ is more intense than the one at 7.45 μ, while for the upper region the 7.45 μ band is the more intense. This is to be expected, for the 6.75 μ band is evidently due to hot CS_2. In the lower part of the flame the combustion is incomplete and hence the hot vapor ought to be more intense than nearer the top. In the present examination the lower part of the flame was used, and the ratio of the intensities of these two bands is still greater than that found by Julius; here the ratio is 34 to 73, while Julius found a ratio of 16 to 22 for the central part of the flame and a ratio of 11 to 8 for the top.

The band at 7.4 μ is in common with the absorption band of SO_2 and since Julius found this band also in burning sulphur, it no doubt belongs to this gas. Then the interesting question arises, "Why is there no emission band at 8.7 μ?" The question must be left unanswered. It is interesting to notice, however, that the 8.7 μ band is found in H_2SO_4, and in sulphates, and appears to belong to the SO_4 ion, while another band found in SO_2 gas at 10.37 μ occurs in fuming H_2SO_4 and has been attributed to SO_3 by Pfund (loc. cit.).

The bands at 2.7 and 4.35 μ are in common with the emission bands of CO_2 and are no doubt due to the combustion of the lamp-wick. This is one of the few examples of the emission of a heated gas during the process of combustion. Water vapor and CO_2 are other examples studied by Rubens and Aschikinass, but in the emission of a flame these are products of combustion. Kayser in his Spectroscopy very aptly remarks that the emission band of methane (CH_4) at 3.3 μ has never been observed in a flame. This is a very weak absorption band,[2] however, and might not appear, just as was found for the 4.6 μ band of CS_2. The 6.75 μ band, which coincides with that of CS_2, was ascribed to COS by Julius, who records its maximum in wave-lengths at 8.48 μ. The 7.45 μ band of SO_2 was thought to be at 10.01 μ. The emission spectra of H_2O and CO_2 have been redetermined by others and need not be mentioned here. It will be sufficient to add that for CO_2 the maximum of emission depends upon the temperature. Whether the SO_2 band at 7.45 μ shifts with change in temperature has not yet been determined. The only other emission band that needs correction is that of HCl at 3.68 μ. A more probable value is 4.05 μ, which is close to the HCl band, found by Ångstrom and Palmer[1] at 3.41 μ (corrected = 3.98).

[1] Ångström and Palmer: Öfversight Kongl. Vet. Akad., No. 6, p. 389, 1893.

APPENDIX IV.

A VACUUM RADIOMICROMETER.

Radiometers having vanes weighing less than 10 mg. are easily affected by earth tremors, so that for general work it is not advisable to reduce the weight much below this amount. Of course, such a moving system is not very sensitive for a short period. For such a vane, with a fiber suspension of such a diameter that the maximum deflection is reached in 15 to 20 seconds, the sensitiveness is not much greater than 9 to 12 cm. deflection per square millimeter surface exposed—the candle and scale each being at a meter's distance. However, a radiometer of such a sensitiveness always gives reliable readings and is to be preferred to a more sensitive instrument which gives larger deflections, but which on account of the lightness of the vanes is affected by earth tremors, temperature changes, etc.

On the other hand, in the radiomicrometer of Boys, the period is governed by the magnetic moment of the moving parts, rather than by the torsion of the fiber suspension, and in nearly all instruments, thus far described, is much shorter than that of the type of radiometer just mentioned. This instrument has received but scant attention since it was first described by Boys, who had a sensitiveness of only about 1 cm. per square millimeter (candle and scale at 1 m.) for a suspension weighing 32 mg. and a period of 10 seconds. He used a window to prevent air currents. Paschen[1] attempted to improve the instrument, but for the best junctions (out of some 50) he could obtain only about three times the sensitiveness of Boys, for a period of about 40 seconds. He then turned his attention to the bolometer, with his well-known success.

The bolometer, however, with a delicate galvanometer requires an elaborate installation, and needs so much attention that the investigator's time is occupied principally with the care of the instrument, which should be a secondary matter in any work.

A great many radiometric investigations do not require the highest attainable sensitiveness (*e. g.*, the author's present work), and in such cases a convenient accessory to a laboratory is a radiometer or a radiomicrometer. The thermopile, of course, also has its place, but here heat conduction, local e. m f.'s, etc., must be contended with.

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[1] Paschen: Ann. der Phys. (3), 48, p. 275, 1893.

The present study of the radiomicrometer was undertaken in connection with the question of the feasibility of combining it with the radiometer, thus developing more energy in the suspended system. The chief difficulty encountered in this combination is to obtain systems which are free from magnetic material. The diamagnetism also plays an important part in this form of thermo-junction, so that the radiometer effect is almost obliterated by the magnetic effect of the coil.

In the radiomicrometer proper the Bi-Sb junction hangs vertically at the axis of the system and hence is not so seriously affected by its diamagnetism, and if the magnet is not too strong a fairly sensitive instrument is obtainable. Since a window improves its steadiness, the whole might as well be in a vacuum, which will eliminate heat conduction, as is well known for thermopiles. By so doing the sensitiveness of a certain system, to be described presently, was increased by at least 70 per cent. By using No. 40 copper wire and bits of Bi and Sb, soldered with Wood's alloy, it is possible to reduce the weight to 10 mg., which, as already mentioned, is a convenient weight for radiometers. The period of such a system will be much less than that of the radiometer of similar weight and time required for maximum deflection.

Before describing the present instrument it will not be out of place to mention some facts concerning tests of sensitiveness of instruments. In previously described instruments no mention is made of the shielding of the thermo-junctions from radiation other than that which falls directly upon the vane, so that the test of sensitiveness is not necessarily a fair one, since reflection from the walls has an enormous effect in increasing the sensitiveness. In fact the indicated sensitiveness may be twice the true value.

In the present instrument (fig. 92), which is a design (similar to that of Boys) for a radiometer, radiomicrometer, or a combination of the two, the receiving surface is directly behind the window, which is covered with an adjustable slit the length of the vane. In this manner no radiation reaches the walls of the instrument, which are black.

The Bi for one part of the junction was obtained by melting the metal between glass or iron plates, which were then pressed together. These thin plates were then cut into strips from 0.15 to 0.2 mm. wide. The Sb part of the junction was split from a large, well-crystallized piece of the metal. These pieces could not be obtained quite so thin as the bismuth. The Bi and Sb pieces were then soldered with Wood's alloy, in the form of a V, to a thin sheet of copper. This is not so good as to have the pieces more nearly parallel, since in the latter case the diamagnetic moment is reduced. The dimensions of the Bi and Sb pieces were about 3.5 by 0.2 by 0.1 mm. The length of the copper loop of No. 40 wire was 4.5

cm., and about 8 mm. in diameter. The area of the thin copper vane was 3 sq. mm. It was blackened by covering it with a little Canada balsam, upon which was dusted fine copper oxide. The weight of the complete loop was less than 10 mg. The magnet was taken from a Weston ammeter. It was used without pole pieces, since the latter

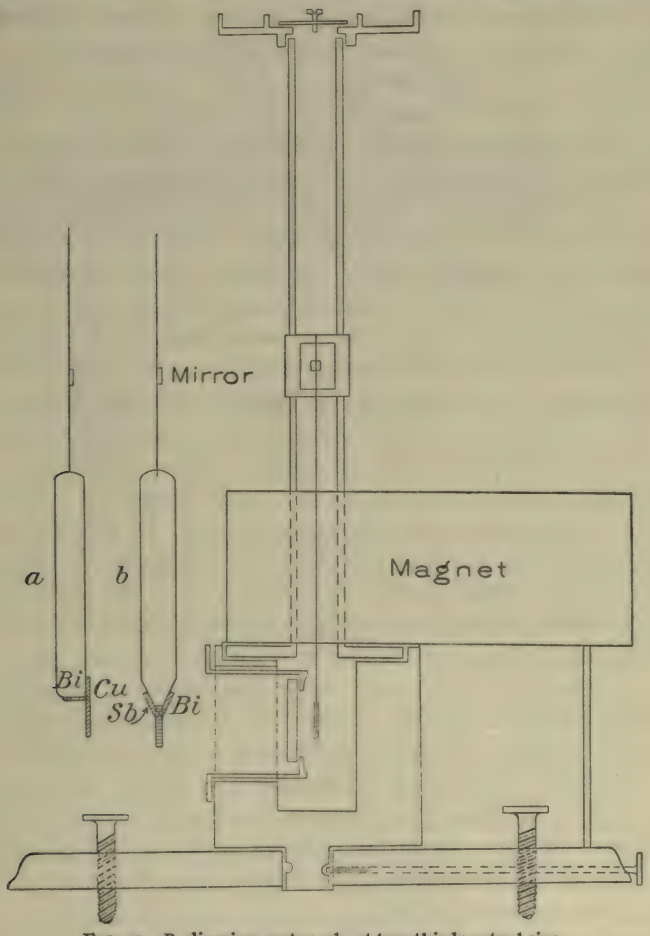

FIG. 92.—Radiomicrometer, about two-thirds actual size.

caused too much damping. The top was covered with the bulb of a thistle-tube, the mouth of which was ground flat. The heavy metal base of the radiomicrometer is of Swedish iron. The narrow vertical tube is of brass. All the joints are made with Kohtinsky cement, except the one at the top and the one containing the support of the rock-salt window. The top seal may be made with mercury. A torsion head

is provided to bring the mirror in any desired position. The loop for the radiometer-radiomicrometer is shown in fig. 92, *a*. The Bi is about 2 by 0.15 by 0.1 mm., soldered to a thin sheet of copper 8 by 0.6 by 0.1 mm. In one case a sheet of mica of the same area was used and extended below the copper sheet, which was then only 2 mm. long. This loop also weighed less than 10 mg. As a radiometer the time required for a maximum deflection was 25 seconds, and its sensitiveness was about 3 to 4 cm. per square millimeter area of vane for a Geryk pump vacuum, which was not high enough for maximum radiometer sensitiveness. This same loop used as a radiomicrometer had a sensitiveness of about 5 cm. deflection per square millimeter area of vane, while its maximum deflection was reached in 8 seconds. The combination of these two was no better than the radiomicrometer, simply because of the fact that the periods were different and the magnetic moment of the radiomicrometer obliterated the radiometer effect. Another loop twice as heavy had a half period (time of maximum steady deflection) of 5 seconds when used either as a radiometer or radiomicrometer. The actual sensitiveness was much lower than in the preceding loops. In this case the radiometer contributed[1] only 15 per cent to the total deflection, while the sensitiveness of the radiomicrometer was increased 50 per cent by placing it in a vacuum.

In fig. 92, *b*, is shown the loop for the radiomicrometer. The dimensions of the Bi-Sb junction are indicated above. Its half-period in air was 20 to 25 seconds, and the deflections in centimeters per square millimeter for meter, candle, and scale were 3.6 cm. On exhausting the instrument with a Geryk pump the half-period dropped to 12 to 14 seconds, while the deflection increased to 5.5 and 6 cm. per square millimeter of exposed area of vane, and as the pumping progressed the sensitiveness continued to rise. The result as a whole indicates that the weight of the moving coil can be reduced to at least one-third of those previously described and that its sensitiveness can be increased by at least 70 per cent by placing the loop in a vacuum. Since a window is used to increase the steadiness, this is no drawback, while in comparison with the type of radiometer having a heavy vane, as already described, it can be given a shorter period.

The purpose in describing this form of instrument is not so much to show the sensitiveness of the present one as to indicate directions in

[1] The method of testing is as follows: The radiomicrometer effect is first found in the air. It is then exhausted and the deflection again noticed. The magnet is then removed and the deflection obtained is due to the radiometer effect. The magnet must of course be placed so that the radiomicrometer deflection is in the same direction as that of the radiometer.

which further improvements are possible. On account of the difficulties in preparing a non-magnetic loop the final word has not been said on the subject of combining the radiometer and the radiomicrometer. At the present writing the best combination was only about 20 per cent more sensitive than the use of the instrument as a radiomicrometer only.

For detecting electric waves the system can be made still lighter, while the heating arrangement can be brought close to the junction.

In conclusion, the fact may be emphasized that in the present test of sensitiveness only that radiation which passed through a slit and fell directly upon the vane was measured. If this precaution had not been taken, the results would have been much higher and would have been as misleading as those obtained by several other investigators.

The sensitiveness of the bolometer varies as the square root of the exposed surface. The writer has found experimentally that the sensitiveness of a radiometer is proportional to the area of the exposed vane, and hence is justified in expressing his results for unit (sq. mm.) area. The use of a candle as a standard is questionable, but since the sensitiveness of the different vanes differs by a factor of from 2 to 25 the candle is a convenient source for comparison.

APPENDIX V.

NOTE ON BLOWING FINE QUARTZ FIBERS.

The bow-and-arrow method of shooting quartz fibers invented by Boys, as well as the method of heating a quartz bead to incandescence in an oxyhydrogen flame and drawing it out into a fine fiber, seems familiar to nearly everyone. Nevertheless, in making rapidly the finest obtainable fibers, such as are necessary for radiometer and for light galvanometer suspensions, there is one step in the latter method which seems a novelty to so many investigators with whom the writer has recently come in contact, that a description, with diagrams, is given here, though there can not be anything new in the process, which seems to be handed down by tradition rather than by recorded history.

Fortunately we can now buy rods of vitreous quartz, and are no longer obliged to build up rods from bits of pulverized quartz crystals by holding them in the hottest part of the oxyhydrogen flame. By the

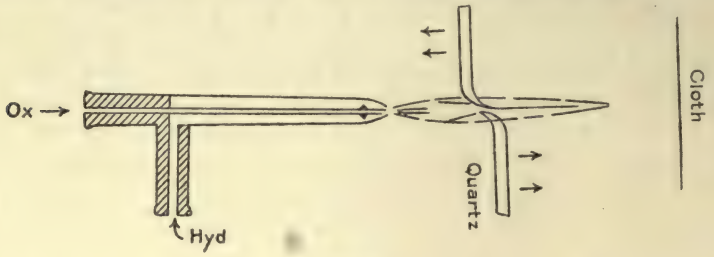

FIG. 93.

following method the manipulator can blow enough fibers in a few minutes to last him many months, provided he stores them in a box away from draughts and flies.

To be brief, the oxyhydrogen or oxy-illuminating gas flame is regulated to a length of 5 to 8 cm. A shallow box (5 by 50 by 100 cm.) with a lid, lined with black canton flannel or simply a black cloth, is placed vertically at a distance of about 35 cm. from the flame, which is horizontal. The manipulator, facing the cloth, holds the rod of vitreous quartz (1 to 2 mm. diameter) in the hottest part of the flame, as shown in fig. 93, which is a horizontal view. When the rod begins to melt it is drawn apart in a horizontal direction, the one end toward, the other end away from the cloth. At the point of rupture a fine fiber will be drawn out by the flame, and the heated gases will drive it against the cloth. The two melted ends are then stroked past each other as rapidly as the manipulator desires, and each time a number of fibers will be drawn out. The fibers are so thin that only the heavier incandescent ones will be seen in the flame and hot gases, but on examining

the cloth in diffuse sunlight at a larger angle of reflection it will be found covered with fibers of various sizes and lengths, the heavier ones, of course, coming from the cooler parts of the flame. Colored spectacles will be found serviceable in this work.

The handling of such fibers requires some dexterity, and in acquiring it the manipulator generally develops some system of his own. The writer has had the best success by employing two flexible glass rods, of about 2 and 8 cm. length respectively, with a bit of shellac solution on one end of each. The quartz fiber is secured from the cloth by means of the longer glass rod, while the shorter one is permitted to hang free from the other end of the fiber. Holding the radiometer or galvanometer suspension in the right hand and the long glass rod in the left, the shellacked end of the suspension is brought against the quartz fiber, close to the long glass rod, which is then turned several times around the suspension. A sudden pull severs the rod from the suspension, leaving the quartz fiber, with the short glass rod at the other end, hanging free. A hot wire is brought near the suspension (now held vertically) to dry the shellac, care being taken that the shellac does not become too hot, otherwise the fiber will drop off. The metal suspension head having previously been laid at one end of a wooden template, which is used to get the exact length of the fiber, the quartz fiber is now laid across this head and the suspension is laid on the template. The short glass rod hangs over the end of the template and draws the quartz fiber taut. The fiber is pressed against the suspension head (previously shellacked), the hot wire is applied, and the task is completed. The manipulator then raises the wooden template into the vertical position, and, if the lint has previously been burned off, the suspension will swing free from it. By proceeding in this manner, which takes less time than required to write this description, no tension greater than the weight of the suspension is brought upon the fiber and rarely is one broken in mounting. A glass tube, of a diameter to hold the metal suspension head, mounted in a wooden block, is serviceable in storing such a suspension and in carrying it from the mounting table to the instrument.

The diameter of such fibers, which of course make excellent cross-hairs, has not been determined, and it will be sufficient to add that they look blue in dim light. The finest fibers appear crinkled, as one removes them from the cloth. The bow-and-arrow process will no doubt produce just as fine fibers, but the present method is better adapted for speed. As already mentioned, the method is not new, but to the writer's knowledge no full description of the actual manipulations involved has been published heretofore, and if this attempt will be of service to any one interested in the subject its mission will be fulfilled.

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